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Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options Volume XIX. Solid Residues Summary Report

Arthur D. Little, Inc., Cambridge, MA

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Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options

Volume XIX
Solid Residues
Summary Report

Interagency Energy/Environment R&D Program Report

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Under EPA Contract No. 68-03-2198, Arthur D. Little, Inc. undertook a study of the "Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options." Some 80 industrial process options were examined in 13 industrial sectors. Results were published in 15 volumes, including a summary, industry prioritization report and 13 industry oriented reports (EPA-600/7-76-034 a through o).

This present report summarizes the information regarding solid residues in the 13 industry reports. Four parallel reports treat sulfur oxides, nitrogen oxides, particulates, and toxics/organics. All of these pollutant oriented reports are intended to be closely used with the original 15 reports.

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ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY-CONSERVING MANUFACTURING PROCESS OPTIONS

Volume XIX. Solid Residues Summary Report

by

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Contract No. 68-03-2198

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment, and even on our health, often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report summarizes information on solid residues from a study of 13 energy-intensive industries. If implemented over the coming 10 to 15 years, these processes and practices could result in more effective utilization of energy resources. The study was carried out to assess the potential environmental/energy impacts of such changes and the adequacy of existing control technology in order to identify potential conflicts with environmental regulations and to alert the Agency to areas where its activities and policies could influence the future choice of alternatives.

The results will be used by the EPA's Office of Research and Development to define those areas where existing pollution control technology suffices, where current and anticipated programs adequately address the areas identified by the contractor, and where selected program reorientation seems necessary.

Specific data will also be of considerable value to individual researchers as industry background and in decision-making concerning project selection and direction.

The Power Technology and Conservation Branch of the Energy Systems-Environmental Control Division should be contacted for additional information on the program.

David G. Stephan
Director
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Cincinnati

ABSTRACT

Under EPA Contract No. 68-03-2198, Arthur D. Little, Inc. undertook a study of the "Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options." Some 80 industrial process options were examined in 13 industrial sectors. Results were published in 15 volumes, including a summary, industry prioritization report, and 13 industry oriented reports (EPA-600/7-76-034 a through o).

This present report summarizes the information regarding sulfur oxide pollutants in the 13 industry reports. Four parallel reports treat nitrogen oxides, particulates, solid residues, and toxics/organics. All of these pollutant-oriented reports are intended to be closely used with the original 15 reports.

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ENGLISH-METRIC (SI) CONVERSION FACTORS

To Convert From	To	Multiply By
Acre	$Metre^2$	4,046
Atmosphere (normal)	Pascal	101,325
Barrel (42 gal)	$Metre^3$	0.1589
British Thermal Unit	Joule	1,055
Centipoise	Pascal-second	0.001
Degree Fahrenheit	Degree Celsius	$t_C^o = (t_F^o - 32)/1.8$
Degree Rankine	Degree Kelvin	$t_K^o = t_R^o/1.8$
Foot	Metre	0.3048
$Foot^3$/minute	$Metre^3$/sec	0.0004719
$Foot^3$	$Metre^3$	0.02831
$Foot^2$	$Metre^2$	0.09290
Foot/sec	Metre/sec	0.3048
$Foot^2$/hr	$Metre^2$/sec	0.00002580
Gallon (U.S. liquid)	$Metre^3$	0.003785
Horsepower (550 ft-lbf/sec)	Watt	745.7
Horsepower (electric)	Watt	746.0
Horsepower (metric)	Watt	735.5
Inch	Metre	0.02540
Kilowatt-hour	Joule	3.60×10^6
Litre	$Metre^3$	1.000×10^{-3}
Micron	Metre	1.000×10^{-6}
Mil	Metre	0.00002540
Mile (U.S. statute)	Metre	1,609
Poise	Pascal-second	0.1000
Pound force (avdp)	Newton	4.448
Pound mass (avdp)	Kilogram	0.4536
Ton (Assay)	Kilogram	0.02916
Ton (long)	Kilogram	1,016
Ton (metric)	Kilogram	1,000
Ton (short)	Kilogram	907.1
Tonne	Kilogram	1,000

Source: American National Standards Institute, "Standard Metric Practice Guide," March 15, 1973. (ANS72101-1973) (ASTM Designation E380-72)

SECTION I

INTRODUCTION

BACKGROUND AND PURPOSE

During 1975 and the first half of 1976, under EPA Contract No. 68-03-2198, Arthur D. Little, Inc., undertook a study of the "Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options" in 13 energy-intensive industry sectors for the U.S. Environmental Protection Agency (EPA). The results of these studies were published in the following reports:

- Volume I -- Industry Summary Report (EPA-600/7-76-034a)
- Volume II -- Industry Priority Report (EPA-600/7-76-034b)
- Volume III -- Iron and Steel Industry (EPA-600/7-76-034c)
- Volume IV -- Petroleum Refining Industry (EPA-600/7-76-034d)
- Volume V -- Pulp and Paper Industry (EPA-600/7-76-034e)
- Volume VI -- Olefins Industry (EPA-600/7-76-034f)
- Volume VII -- Ammonia Industry (EPA-600/7-76-034g)
- Volume VIII -- Alumina/Aluminum Industry (EPA-600/7-76-034h)
- Volume IX -- Textiles Industry (EPA-600/7-76-034i)
- Volume X -- Cement Industry (EPA-600/7-76-034j)
- Volume XI -- Glass Industry (EPA-600/7-76-034k)
- Volume XII - Chlor-Alkali Industry (EPA-600/7-76-034l)
- Volume XIII -- Phosphorus/Phosphoric Acid Industry (EPA-600/7-76-034m)
- Volume XIV -- Copper Industry (EPA-600/7-76-034n)
- Volume XV -- Fertilizer Industry (EPA-600/7-76-034o)

In the course of this study, some 80 industrial processes were examined as potential energy-conserving options, focusing on:

- Identification of any major sources of amounts of pollutants (air, water, and solid) expected from the processes;

- Development of estimated capital and operating costs for both production and pollution control aspects of the processes;

- Estimation of the types and amounts of energy used in both production and pollution control for the processes;

- Assessment of the economic viability and likelihood of implementation of those alternative process options being studied;

- Identification of areas where EPA's activities and policies could influence the future choice of alternatives; and

- Identification of research and development areas in both process and pollution control technology.

Because of the industry orientation of the study, encompassing 15 volumes and some 1,700 pages, we felt that pollutant-specific information across all the 13 sectors studied should be summarized. Five such pollutant-specific areas were identified to be of particular interest:

- Nitrogen oxide (NO_x) emissions,

- Sulfur oxide (SO_x) emissions,

- Fine particulate emissions,

- Solid residues, and

- Organic and/or toxic pollutants.

A summary pollutant report in each of these areas has been prepared. Although some estimates and extrapolations of pollutants have been attempted where the information was readily available, we have not in general attempted to go beyond the 15 original reports.

APPROACH

These summary pollutant reports are intended to be used closely with the original 15 reports. Generally, information such as detailed descriptions of the processes which can be found in the previous 15 reports has not been duplicated in the 5 pollutant reports, but has been extensively referenced by volume number and page number (e.g., Vol. VII, page 20, refers to page 20 of the Ammonia Industry report).

In Section II of this report (Findings and R&D Overview), summary information on generic, cross-industry solid residue problems that emerge and suggestions for research and development work in the areas of both pollution control technology and process technology are presented. All

emissions are estimated unless specifically referenced, since we believe that actual data do not exist for the processes described, which are frequently still under development.

To give the reader a sense of the size of the industries for which the pollution problems covered in these summary pollutant reports are considered, Table 1 lists these industries, their total production in 1974 (the base case year for the study) and their projected incremental production in 1989 -- 15 years hence. In the following sections and tables, solid-residue loads calculated for 1989 are based on the assumption that the individual process option accounts for incremental production.

TABLE 1. PROJECTED U.S. PRODUCTION IN INDUSTRIES STUDIED

Commodity	Total U.S. Production in 1974 (10^6 tons*)	Projected Rate of Growth (%/yr)	Total Projected Production in 1989 (10^6 tons)	Increase in Annual Production in 1989 over that of 1974 (10^6 tons)
Alumina	7.7	6.0	18.5	10.75
Aluminum	5.0	6.0	12.0	7.0
Ammonia	9.2	6.0	22.0	12.8
Cement	79.0	2.0	106.3	27.3
Chlorine	11.0	5.0	22.9	11.9
Coke	62.0	2.5	89.8	27.8
Copper	1.6	3.5	2.7	1.1
Fertilizers (HNO_3)	8.2	4.0	14.8	6.6
Glass (flat)	29.0	2.5	42.0	13.0
Iron	100.0	2.5	144.8	44.8
Olefins (ethylene)	13.0	8.0	41.2	28.2
Petroleum	740.0**	1.5	925.0***	185.0****
Pulp (kraft)	16.0	5.0	33.5	17.3
Pulp (newsprint)	3.9	2.5	5.6	1.7
Phosphoric Acid (detergent grade)	1.4	2.5	2.03	0.63
Phosphoric Acid (wet acid grade)	9.0	2.5	13.0	4.0
Steel	133.0	2.5	193.0	60.0
Textiles (knit)	0.32	2.2	0.44	0.12
Textiles (woven)	2.1	2.2	2.91	0.81

*All tons referred to in these reports are net tons, unless otherwise indicated.

**Approximate equivalent of 30 quads (1 quad is equal to 10^{15} Btu).

***Approximate equivalent of 37.5 quads.

****Approximate equivalent of 7.5 quads.

SECTION II

FINDINGS AND R&D OVERVIEW

FINDINGS

Of the 13 industries studied, 6 have potentially applicable process options that would result in a significant change (more than 3×10^6 ton/yr) in the base case solid-residue generation rate. These process options, if adapted in new plants, would result in the following changes in estimated solid residues discharged:

- Iron and Steel Industry - direct reduction (increase of 15.5×10^6 ton/yr)
- Cement Industry - fluidized bed process (decrease of 3×10^6 ton/yr)
- Aluminum Industry - use of domestic clays for alumina production (increase of 7.5 to 27×10^6 ton/yr)
- Pulp and Paper Industry
- Phosphoric Acid (detergent grade) - wet process acid with chemical clean-up (increase of 3×10^6 ton/yr)
- Copper Industry - Arbiter process (increase of 3×10^6 ton/yr)

Process options for the textile, fertilizer and pulp and paper industries, (excluding the production of newsprint) have very little impact when compared with the base case solid-residue generation rate.

All of the remaining industries have at least one process option that would result in a significant increase in the base case solid-residue generation rate. The most common cause of the increased generation of solid residues is the conversion from natural gas or fuel oil to coal as the primary raw material and/or process energy source. The major solid-residue streams associated with the use of coal ash, flue gas desulfurization sludge, and related wastewater treatment sludge. In some of these cases, the bulk of the solid-residue load can be, or is generated, at an electric utility, such as in electric melting for glass, while in others, such as coal gasification or hot gas generation for glass melting, the coal must be used on-site. It should, therefore, be borne in mind that a shift from gas or oil to coal at the power plant would generate a comparable increase in the solid-residue load, consisting of coal ash (0.105 lb/kWh), and, eventually, SO_x scrubber sludge (0.25 lb/kWh). Solid-residue discharges from electric utility power plants have not been estimated in this study.

In the alumina industry, process options designed to alleviate U.S. dependence on imported bauxite by extracting alumina from domestic kaolin clay would result in both a significant increase in the base case solid-residue generation rate and a significant change in the chemical composition of the waste. In the copper industry, the use of the Arbiter hydrometallurgical process for extracting copper from ore would result in a substantial increase in the base case generation of solid waste.

For most of the process options that result in a significant increase in solid-residue generation, there is very little potential for decreasing the amount of solid waste by either in-plant controls or by further processing of the waste streams. This is particularly true when the solid-residue results from the use of coal. Solid residues of an organic nature, such as certain waste streams associated with process options in the petroleum refining, olefins, pulp and paper, and textile industries, could be greatly reduced in volume by incineration.

Finally, there is another group of process options which do not appear to have a significant impact on solid-residue generation. For these, other factors (energy savings, cost, water pollution, etc.) will determine the extent to which the process is implemented over the coming years.

A comparison of solid-residue generation rates (and resultant incremental solid-residue quantities based on the growth period from 1974 to 1989) for the base case manufacturing technology and its process options is presented in Table 2. Although it would be unrealistic to presume that all incremental production over the next 15 years would incorporate any one of the specified processes, it would be equally unrealistic to try to estimate the fraction of the production which might use an individual process. Therefore, in an effort to present to the reader the perspective of the changes which might occur, we have compiled in Table 2 the solid-residue outputs which would be generated, assuming utilization of the designated process option for all incremental production in 1989 over that produced in 1974.

It should be recognized that the figures given in Table 2 are related to incremental production. For example, the 9.0×10^6 tons of solid waste expected in 1989 from the BOP is derived from the incremental production in that year, 60×10^6 tons. The total solid-residue production from the BOP would be 21×10^6 tons, from 190×10^6 ton of steel, based on the increment plus 62% discharge factor of 150 lb/1000 lb. Use of the proposed option -- off-gas recovery -- does not reduce solid residue in this case, but does offer other energy and air pollution advantages.

Similarly, assuming all iron is obtained by the blast furnace, the total incremental production of solid waste in 1989 would be 20×10^6 ton of iron. Use of the option process -- external desulfurization --

TABLE 2. SUMMARY OF ESTIMATED SOLID-RESIDUE DISCHARGES

Commodity	Process	Solid Residue Discharge from Base Case Process-1974 (10^6 ton/yr)	Solid-Residue Discharge-1989*++ (10^6 ton/yr)	Change in Solid Residues from Base Case-1989
Coke	Base Case: Wet quenching of coke	N/A	N/A	N/A
	• Dry quenching of coke	N/A	N/A	N/A
Steel	Base Case: No off-gas recovery	12.3	9.0	--
	• Off-gas recovery	--	9.0	0.0
Blast Furnace Hot Metal	Base Case: Blast furnace	14.0	6.3	--
	• Blast furnace with external desulfurization	--	4.7	-1.6
Steel (integrated)	Base Case: Steelmaking coke oven and blast furnace BOP route	24.6	18.0	--
	• EAF route	--	33.5	+15.5
Petroleum	Base Case: East Coast refinery model	1.53++	0.38++	--

(continued)

TABLE 2. (continued)

Commodity	Process	Solid Residue Discharge from Base Case Process-1974 (10^6 ton/yr)	Solid-Residue Discharge-1989*++ (10^6 ton/yr)	Change in Solid Residues from Base Case-1989
Petroleum (continued)	• Direct combustion of asphalt	--	0.38++	0.0
	• Flexicoking	--	0.74++	+0.36
	Base Case: Gulf Cost refinery model	1.53++	0.38++	--
	• On-site electric power by asphalt combustion	--	0.38++	0.0
	Base Case: West Coast refinery model	1.53++	0.38++	--
	• Hydrocracking of Heavy Bottoms	--	0.39++	+0.01
	• High Purity Hydrogen by partial oxidation	--	0.40++	+0.02
	• Flexicoking	--	0.742	0.359
	• On-site electric power by combustion of vacuum bottoms	--	0.383	0.0

(continued)

TABLE 2. (continued)

Commodity	Process	Solid Residue Discharge from Base Case Process-1974 (10^6 ton/yr)	Solid-Residue Discharge-1989*+ (10^6 ton/yr)	Change in Solid Residues from Base Case 1989
Petroleum (continued)	• High-Purity hydrogen via partial oxidation of asphalt	--	0.403	0.020
Pulp & Paper	(Solid-residue streams unquantified)			
Olefins	Base Case: Ethane-propane process	0.0205	0.0442	--
	• Naphtha process	--	0.0764	+0.0322
	• Gas-oil process	--	0.1394	+0.0952
Ammonia	Base Case: Ammonia via natural gas	--	small (unquantified)	--
	• Ammonia via coal gasification	--	3.01	+3.01
	• Ammonia via heavy fuel oil	--	0.019	0.019
Alumina	Base Case: Bayer process	6.160	8.600	--
	• Hydrochloric acid ion exchange	--	36.000	+27.4

(continued)

TABLE 2. (continued)

Commodity	Process	Solid Residue Discharge from Base Case Process-1974 (10^6 ton/yr)	Solid Residue Discharge-1989*+ (10^6 ton/yr)	Change in Solid Residue from Base Case 1989
Alumina (continued)	• Nitric acid ion exchange	--	20.400	+11.8
	• Clay chlorination (Toth) alumina	--	16.1	+7.5
Aluminum	Base Case: Hall-Heroult (current practice, C.P.)	0.1125	0.158	--
	• Hall-Heroult (new)	--	0.158	0.0
	• Alcoa Chloride	--	2.000	1.842
	• Refractory hard-metal cathode	--	0.158	0.0
	Base Case: Bayer with Hall-Heroult (C.P.)**	7.81	10.92	
	• Clay Chlorination (Toth Alumina) and ALCOA Chloride	--	22.33	11.41
Textiles	(Minor solid-residue-unquantified)			

(continued)

TABLE 2. (continued)

Commodity	Process	Solid Residue Discharge from Base Case Process-1974 (10^6 ton/yr)	Solid Residue Discharge-1989*+ (10^6 ton/yr)	Change in Solid Residue from Base Case 1989
Cement	Base Case: Long dry kiln	11.85	4.1	--
	• Suspension preheater	--	1.75	-2.345
	• Flash calciner	--	1.75	-2.345
	• Fluidized bed	--	0.820	-3.275
	• Coal as fuel instead of gas in long dry kiln	--	4.1 - 5.7	0.0 - +1.60
Flat Glass	Base Case: Regenerative furnace	0.290	0.130	--
	• Coal gasification	--	0.650	+0.520
	• Direct coal firing	--	1.222	+1.092
	• Coal-fired hot-gas generation	--	0.858	+0.728
	• Electric melting	--	0.611	+0.481
	• Batch preheat with natural gas firing	--	0.130	0.0

(continued)

TABLE 2. (continued)

Commodity	Process	Solid Residue Discharge from Base Case Process-1974 (10^6 ton/yr)	Solid Residue Discharge-1989*+ (10^6 ton/yr)	Change in Solid Residues from Base Case 1989
Chlorine, NaOH	Base Case: Graphite-anode diaphragm cell	0.736	0.796	--
	• Dimensionally stable anodes	--	0.764	-0.032
	• Polymer modified asbestos	--	0.762	-0.034
	• Polymer membrane	--	0.762	-0.034
	• Ion exchange membrane	--	0.762	-0.034
	• Expandable DSA	--	0.762	-0.034
	• Mercury cell	N/A	N/A	N/A
Phosphoric Acid (Detergent Grade)	Base Case: Electric furnace	0.476	0.214	--
	• Chemical clean-up of wet-process acid	--	3.219	+3.005
	• Solvent extraction of wet-process acid	--	0.573	+0.359

(continued)

TABLE 2. (continued)

Commodity	Process	Solid Residue Discharge from Base Case Process-1974 (10^6 ton/yr)	Solid-Residue Discharge-1989*+ 10^6 ton/yr)	Change in Solid Residues from Base Case 1989
Copper	Base Case: Conventional smelting	4.976	3.420	--
	• Outokumpu flash smelting	--	3.420	0.0
	• Noranda	--	3.420	0.0
	• Mitsubishi	--	3.420	0.0
	• Arbiter	--	6.380	+2.96
Fertilizers	Base Case: Nitric acid manufacturing w/o NO_x control	negligible	--	--
	• Nitric acid manufacturing w/NO_x control			
	• Catalytic reduction	negligible	--	0.0
	• Molecular sieve	negligible	--	0.0
	• Grand Paroisse	negligible	--	0.0
	• CDL/Vitak	negligible	--	0.0
	• Masar	negligible	--	0.0

(continued)

TABLE 2. (continued)

Commodity	Process	Solid Residue Discharge from Base Case Process-1974 (10^6 ton/yr)	Solid Residue Discharge-1989*+ (10^6 ton/yr)	Change in Solid Residues from Base Case 1989
Fertilizers (continued)	Base Case: Mixed fertilizer plant w/natural gas firing	negligible	0.0	--
	• Better equipment technique with fuel oil	negligible	0.0	--
	• Conversion from natural gas to fuel oil (installing scrubbers)	--	0.0125	+0.0125

*Based on incremental production from the year 1974 to 1989 derived from anticipated growth rates (Table 1).

+Based on the assumption that all increased production would be from the designated process.

**Based on 1.93 tons alumina per ton aluminum.

++Assumes all refinery output on a national basis is by processes indicated.

N/A = Not available.

only for the incremental production volume, would reduce the total solid residue generated to 19 x 10^6 ton/yr in 1989.

All of these options which occur in very large-volume industries having major impact on the nation's industrial energy use, offer the opportunity to reduce significantly both energy use and solid-residue generation without creating problems in the air or water environment.

These numbers perhaps become more meaningful or significant when one realizes that a single 100 mw coal-fired power plant now generates 46 x 10^3 ton/yr of coal ash and fly ash and will, with the addition of SO_2 control by lime scrubbing, add an additional 110 x 10^3 ton/yr to give a total of 156 x 10^3 ton/yr.

Further comparisons which can be made are that 4.7 x 10^6 ton/yr (1972) of municipal sludge and 125 x 10^6/1971 ton/yr of solid residue are generated in the United States annually.

Examination of the last column in Table 2 shows that compared to the base case processes, the greatest reduction in tons of solid-residue discharges per year can be achieved by selective implementation of new processes in:

- Iron and Steel Industry (external desulfurization 25% decrease)
- Cement Industry (kiln with suspension preheater 57% decrease) flash calcining (57% decrease) and fluidized bed cement process (80% decrease), and
- Pulp and Paper Industry -- de-inking of old newspaper for newsprint resulting in a 5.6 x 10^6 ton reduction as a potential waste is used as raw material in 1989 (see Table 1).

Process changes in some of the industries shown in Table 2 may be implemented because of feedstock shortages (e.g., manufacture of olefins from naphtha rather than natural gas), and fuel switching (e.g., use of coal in cement making). In other cases, processes may be developed for other reasons, such as development of a domestic alumina industry based on indigenous kaolin clays. Such a process, based on using coal to the extent possible, would result in significantly higher solid-residue discharge than a Bayer plant based on natural gas, as described in the Alumina/Aluminum Industry report. Although the estimated change in emissions listed in Table 2 was based on incremental capacity from 1974 to 1989 only, in some cases an alternative process, or a process modification, may replace existing capacity. For example, in the aluminum industry, refractory hard metal cathodes may be installed in existing Hall-Heroult cells. The application of alternative processes to existing plant capacity will increase the potential effect on solid-residue dis-

charges compared to the estimated effect shown in Table 2. Further perspectives in each of these industry sectors with descriptions of the processes can be obtained from the individual industry sector reports (Volumes III through XV).

Should U.S. industry expand using current (base case) technology, Table 3 shows that estimated solid-residue discharges in 1989 would increase by 35.8×10^6 tons per year compared to discharges of 12.5×10^6 ton per year of solid residue generated in 1971. However, if all U.S. industry expanded by implementing the technologies considered here that discharged the largest solid residues, Table 3 shows that the increases in solid-residue discharges in 1989 would be 91.9×10^6 ton per year, some 154% higher than using conventional technology. On the other hand, if industry expanded by implementing the least solid-residue discharging technology, solid-residue discharges in 1989 are calculated to decrease by 3.3×10^6 ton/yr, some 9% less than by conventional technology. If the national production growth rate projections shown in Table 1 are accurate, then calculated emissions will probably lie somewhere between these extremes. Thus, implementation of such new technologies as considered here can significantly impact solid-residue discharges in the industrial sector.

Table 4 shows our estimate of the types of processes likely to be installed in the time period up to 1989 with the related solid-residue discharges from new plants calculated for the year 1989 assuming no retirement of existing facilities. For example, a reading of the industry reports shows that in the cement sector incremental cement capacity will be effected by preheaters, coal firing, etc. If such capacity is installed, anticipated annual solid-residue discharges in 1989 would be 0.82×10^6 to 1.75×10^6 ton/yr (Table 4) compared to the 4.095×10^6 ton/yr if conventional rotary kiln technology were employed. Similar judgments were made in other sectors to arrive at total calculated annual solid-residue discharges of 44.75×10^6 to 69.915 ton/yr (Table 4) emitted in 1989 from new plant capacity installed in the period 1974-1989.

IDENTIFICATION OF CROSS-INDUSTRY TECHNOLOGY

As specifically related to the problem of solid residues, the only cross-industry energy-conserving technology that has a significant impact on the nature and quantity of solid residue is the conversion from natural gas or fuel oil to coal.

R&D AREAS

With regard to solid residues emanating from new technology investigated in this study, the following have been identified as deserving R&D attention:

TABLE 3. ESTIMATED INCREASE IN ANNUAL SOLID RESIDUE DISCHARGES (1989-1974) ASSUMING INDUSTRY EXPANDS USING PROCESS TYPES INDICATED (10^6 Tons Solid Residue/yr)

Commodity (Vol No)*	Base Case Process	Using Process With Largest Potential Discharges	Using Process With Smallest Potential Discharges
Steel (III)	18.0	33.5	18.0
Petroleum+(IV)	0.383	0.742	0.383
Kraft Pulp (V)	---small, not quantified---		
Newsprint Pulp (V)	5.6	5.6**	0.0
Olefins (VI)	0.0442	0.1394	0.0442
Ammonia (VII)	small	3.01	small
Alumina (VIII)	8.6	36.0	8.6
Aluminum (VIII)	0.158	2.0	0.158
Textiles-Knit (IX)	---small, not quantified---		
Textiles-Woven (IX)	---small, not quantified---		
Cement (X)	4.095	4.095	0.82
Flat Glass (XI)	0.130	1.222	0.130
Chlorine, NaOH (XII)	0.796	0.796	0.762
Phosphoric Acid (XIII)	0.214	3.219	0.214
Copper (XIV)	3.42	6.38	3.42
Fertilizers (HNO_3) (XV)	small	0.0125	small
TOTAL	35.840	91.111	32.531

* Volume Number of Industry Report

**Estimated newsprint pulp production in 1989 (see Table 1).

+Assumes selected regional refinery model applies nationally.

TABLE 4. ESTIMATED RANGE IN SOLID RESIDUE DISCHARGES IN 1989 FOR NEW PROCESSES LIKELY TO BE IMPLEMENTED

Commodity (Vol No)*	Likely Types of Processes to be Implemented in New Plants	Calculated Range in Annual Discharges for Plan Capacity (1989-1974) (10^6 ton/yr)
Steel (III)	Coke oven, Blast Furnace, BOP(c),(b)	18.0 - 18.0
Petroleum (IV)	Hydrocracking, flexicoking, etc.	0.38 - 0.74
Kraft Pulp (V)	Kraft, Rapson, Alakline-oxygen	small
Newsprint Pulp (V)	RMP, TMP, De-inking	0.0 - 5.6
Olefins (VI)	Naphtha, gas oil	0.076 - 0.14
Ammonia (VII)	Heavy fuel oil, coal	0.019 - 3.01
Alumina(a) (VIII)	Bayer, leaching domestic clays	20.4 - 36.0
Aluminum(a) (VIII)	Hall-Heroult, aluminum chloride(a)	0.16 - 2.00
Textiles, Knit (IX)	Advanced aqueous, solvent	small
Textiles, Woven (IX)	Advanced aqueous	small
Cement (X)	Preheaters, coal firing	0.82 - 1.75
Flat Glass (XI)	Regenerative furnaces, preheaters electric furnaces	0.13 - 0.86
Chlor-alkali (XII)	Dimensionally stable anodes, new membranes	0.76 - 0.76
Phosphoric Acid: Detergent grade (XIII)	Wet acid cleanup	0.57 - 3.22
Copper (XIV)	Oxygen or flash processes(b)	3.42 - 3.42
Fertilizers-Mixed Fertilizer Plant	Fuel Oil	0.013 - 0.013
TOTAL		44.8 - 75.5

*Volume Number of Industry Report.

(a) A significant fraction of the incremental U.S. demand is expected to be imported.

(b) In addition, electric furnaces are expected to be installed based at least partially on scrap.

(c) With collection of CO from BOF's.

(d) Assumes East Coast refinery model applies nationally.

- Demonstration of adequate landfill disposal techniques. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the industry assessment reports dealing with aluminum, cement, iron and steel, petroleum refining, and phosphorus. To a lesser extent, it is also a problem in the ammonia, chlor-alkali, copper, glass, olefins, pulp and paper, and textile industry sectors.

- Demonstration of thermal destruction technologies for organic wastes. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the industry assessment reports dealing with aluminum, olefins, and petroleum. To a lesser extent, it is also a problem in the chlor-alkali, iron and steel, and pulp and paper industry sectors.

- Additional research into the methods of categorization, regulation and legal methodologies for controlling the disposal of solid residues. Further information on the source of pollutants and nature of the problems in new technology examined in this study is found in the industry assessment reports dealing with aluminum, ammonia, cement, copper, fertilizers, glass, iron and steel, olefins, petroleum refining, and phosphorus. To a lesser extent, it is also a problem in the chlor-alkali, pulp and paper, and textile industry sectors.

Thus in each case, the direction of research programs should be viewed with the objective of attaining the maximum effectiveness for removal or controlling pollutants at the minimum economic penalty, since it is rarely possible to remove or control pollutants to present and anticipated standards without entailing cost penalties. Consequently, research programs must be examined within the framework of cost/benefits to the environment, to health, and to the economy. Unfortunately, it is not yet possible to determine the impact of the Resource Conservation and Recovery Act of 1976 on needed research and development programs.

SECTION III

PROCESSES AND SOLID-RESIDUE DISCHARGES

In Volume II (page 19) in which we described the methodology used in this study, we indicated that selected State air emission regulations, along with the Federal Government's stationary source performance standards and effluent limitation guidelines, were surveyed to:

- establish the most probable limits of air and water emissions, and
- obtain a perspective of the types of pollution control systems to be considered.

While there are a large number of different regulations for airborne emissions at the State regulatory level, we found that approximately the same type of air pollution control systems would be required, regardless of the State or Federal regulations to be met. Generally, these air pollution control systems included bag houses, venturi scrubbers, and electrostatic precipitators for particulates and chemical-based systems for sulfur removal, such as alkaline-based aqueous scrubbing for SO_x.

For water effluents we chose the EPA's best available technology economically achievable (BATEA) guidelines (1983) as the effluent limitations that would have to be met for both currently practiced and alternative processes considered. The rationale for this choice was that any plant employing the technologies evaluated in these reports should install wastewater treatment systems capable of meeting BATEA standards, although at the time of construction the new source performance standards might be applicable. Because regulations for the handling and disposal of solid residues are either non-specific or non-existent, we chose various types of controlled landfill disposal methods, where our judgment suggested potential adverse environmental impacts might occur from uncontrolled disposal.

Solid residues resulting from dust collection, water pollution control, and industrial process discharges (e.g., slags, slimes, and so on) as described in the industry reports (Volumes III through XV) are summarized in this section.

IRON AND STEEL INDUSTRY

Basic Oxygen Process (BOP) for Steelmaking

Base Case Solid-Residue Disposal--

The base case BOP unit (which is described in detail in Volume III, pages 18-28) is a complete combustion system in which the gases issuing from the mouth of the furnace are burned and collected in a hood with considerable infiltration of air, and then cooled and cleaned of particulates before being released to the atmosphere. There are two significant solid-residue streams associated with BOP operations: (1) slag and (2) wet sludge resulting from dust collection.

Neither the composition nor the quantity of the slag is affected by the process changes selected for analysis in the original study; therefore, its disposal was not a subject of comparison in the study. The ultimate fate of BOP slag (as well as slag from other steelmaking processes) proceeds along three routes: (1) some of the slag is recycled back to the blast furnace; (2) some of it is sold to slag processors where it is made into aggregate material for construction uses; and (3) a portion is disposed of in landfills on or near the plant site.

Most BOP units employ wet high-energy scrubbers for dust collection. About 55 lb of dust are produced per ton of steel in the BOP. The dust-laden scrubber water is usually subjected to suspended solids removal in a sedimentation basin or clarifier. A portion of the water is discharged. The suspended solids, i.e., the BOP dust, are removed from the clarifier as a wet sludge. This sludge is sometimes subjected to mechanical dewatering to further reduce its volume prior to reclamation of iron values and/or disposal.

The ability to reclaim iron values depends upon the composition of the dust, which is influenced by the nature of the scrap charged to the BOP. If clean, uncoated home scrap is used, the dust consists primarily of iron oxides and can be recycled to the sinter strand. If purchased scrap is used, it may not be possible to control the composition closely; as a result, the dust and resultant sludges can contain lead, zinc, tin, and other metals.

When the sludge cannot be recycled, suitable care has to be taken in its disposal. Because of its heavy metal content (mostly in the form of oxides and hydroxides), special attention should be given to preventing acidic leaching conditions from occurring, and appropriate efforts should be taken to mitigate percolation and run-off from the disposal site.

Process Option 1 - BOP Off-Gas Recovery Process Alternative--

When off-gas recovery is incorporated into a BOP unit, the carbon monoxide containing off-gas is either collected for eventual use as an internal plant fuel as in the conventional BOP, or flared which results in oxidizing the off-gases at the flare rather than at the mouth of the vessel.

BOP units equipped with off-gas recovery equipment produce lower gas volumes than convetional BOP units, due to the marked reduction in the volume of infiltration air. Gas-cleaning equipment in both cases consists of high-energy venturi scrubbers. The quantity of dust is essentially the same for conventional and off-gas-recovery-equipped BOP units. The composition of the dust, however, is slightly different.

In the conventional BOP operation where the carbon monoxide is burned with entrained air, the dust particules are largely oxidized. In BOP units equipped with off-gas recovery, the dust is subjected to far less oxidation and, therefore, contains a higher fraction of unoxidized or partiallly oxidized species. A comparison of the composition of BOP dust from conventional units and units equipped with off-gas recovery is shown in Table 5 (Volume III, page 25).

The use of off-gas recovery in the basic oxygen process for steelmaking will have virtually no effect on the volume of solid residues produced ($\sim$ 150 lb/ton of steel). See Volume III, page 72.

No new chemical constituents are introduced into the solid-residue stream. However, since there is less oxidized iron in the solid residues from BOP units equipped with off-gas recovery, it is reasonable to expect that the unoxidized or partially oxidized iron will slowly undergo oxidation once deposited in a disposal site. The oxidation process could exert a minor oxygen demand on water percolating through the waste. However, we do not view this as a significant environmental problem.

The Conventional Blast Furnace for the Production of Iron

Base Case Solid-Residue Disposal--

The base case process is the conventional blast furnace used in the production of iron. A blast furnace produces two major solid-residue streams: (1) slag and (2) wastewater treatment sludge. (This process is described in Volume III, page 29-31.) A large fraction of the slag generated by blast furnaces is sent to slag processors where it is converted into construction aggregate material. When the demand for slag is less than the supply, the excess slag must be disposed of on land.

Blast furnaces are equipped with air pollution control systems that employ wet scrubbers for the removal of particulate matter. The scrubber water is subjected to gravity settling. Part of the effluent from the gravity settling step is recycled back to the scrubbers, while the remainder is discharged. Future water pollution regulations may require that the water thus discharged be subjected to further treatment steps for the removal of selected pollutants. The particulate matter originally present in the blast furnace gas is removed from the clarifier as a wet sludge. The volume of the sludge is often reduced by mechanical dewatering operations.

TABLE 5. COMPARISON OF BOP DUST COMPOSITIONS
(weight percent)

	Conventional BOP	BOP with Off-Gas Recovery
Ke Total	59	75
Ke Metal	-	10
Ke as FeO	1.6	62
Ke as Fe_3O_4, Fe_2O_3	57.4	3
CaO	2	2
SiO_2	1	1

While the solid phase of the sludge is relatively innocuous (containing mostly carbon and iron particles), the liquid fraction typically contains such pollutants of concern as phenol, cyanide, sulfide, ammonia, fluoride, and certain trace heavy metals. For this reason, care should be taken to dispose of the sludge in a manner that will preclude groundwater contamination. A portion of the dewatered wastewater treatment sludge is usually recycled back into the process for reclamation of iron values.

Process Option 1 - External Desulfurization Alternative--

Coke, which contains some of the sulfur found in the coal used is the major contributor to the total amount of sulfur entering the blast furnace. Other sources of sulfur in the blast furnace include fuel injections, the scrap mixed with the burden, and the minerals themselves (ore, limestone).

Only a negligible portion of the sulfur is found in the off-gases; most of the sulfur leaving the blast furnace appears in the liquid slag and hot metal. Thus, there is a certain degree of "internal" desulfurization inherent in the process. The capacity of the slag to retain sulfur is generally increased as more limestone is added. Limestone, however, increases coke consumption which, in turn, introduced more sulfur. Clearly, then, there is a limit to the amount to which this "internal" desulfurization is viable. It may be advantageous to tap a hot metal containing more sulfur than specified, and to add to the process sequence a new step, viz., the injection of desulfurization agents into the molten iron during its transfer from the blast furnace to the steelmaking furnace. These agents (usually magnesium or calcium compounds) react with the dissolved sulfur and form a sulfide slag that can be disposed of. This additional step is called external desulfurization.

External desulfurization can provide two energy-related benefits: (1) it can reduce the coke consumption, and (2) more importantly, it decreases the dependence on low-sulfur metallurgical coal, which is becoming increasingly difficult to obtain.

The external desulfurization process reduces the amount of coke and limestone used in the blast furnace, thereby reducing the amount of slag generated in the blast furnace proper. While external desulfurization produces a slag stream of its own, the overall effect is a net reduction in the amount of slag generated.

The external desulfurization process produces a gaseous effluent which, when subjected to wet scrubbing, will produce a wastewater and resultant wastewater treatment sludge stream, not unlike that of the parent blast furnace. Again, the additional wastewater treatment sludge stream, from the external desulfurization step must be balanced against the reduced voluem of blast furnace gas and associated particulate matter and resultant sludge.

The overall effect of external desulfurization on the making of iron in a blast furnace is a net reduction in the total quantity of solid residues of approximately 25% (Volume III, page 40). The composition of the solid residue is expected to be essentially unaltered and, consequently, disposal procedures also remain the same.

The Quenching Operation in Coke Making

Process Option 1 - Dry Quenching vs. Conventional Wet Coking Alternative--

This energy-saving alternative is designed to reclaim the heat that is lost during the base case practice of quenching coke with water. Neither the base case wet quenching nor the alternative of dry quenching produce a solid-residue stream that is destined for ultimate land disposal. There are, therefore, no solid-residue disposal implications associated with the implementation of dry quenching of coke.

Conventional Iron and Steelmaking Base Case for Comparison with Direct Reduction of Iron Ore

Base Case Solid-Residue Disposal--

Direct reduction of iron ore is designed to replace the blast furnace along with its supporting coke plant. In the version of the direct reduction process selected for comparison, the reduced product iron from the direct reduction unit is sent to an electric arc furnace (rather than a more conventional open-hearth or basic oxygen process furnace) for steelmaking. To compare direct reduction with the existing technology on an equivalent basis, it is necessary to make the comparison all the way through the steelmaking process. Thus, the base case process consists of the following units:

- Byproduct coke plant,
- Blast furnace, and
- Basic oxygen process (BOP) furnace.

The major solid-residue streams from the base case process operations are described below (Volume III, page 72):

- Byproduct Coke - solid residues includes coke dust and wastewater treatment sludge generated at a rate of approximately 0.0077 ton/ton of steel.

- Blast Furnace - solid residues include furnace slag and wastewater treatment sludge, generated at a rate of approximately 0.14 ton/ton of steel;

- Basic Oxygen Furnace - solid residues include furnace slag and wastewater treatment sludge, generated at a rate of approximately 0.15 ton/ton of steel.

The total solid-residual generation rate for the base case process is the sum of the above streams, or approximately 0.30 ton/ton of output.

The composition and ultimate disposal of wastewater treatment sludge were discussed in the previous section of this report dealing with BOP off-gas recovery and external desulfurization of blast furnace hot metal. Byproduct coke plant wastewater treatment sludge deserves mention, however. The wastewater from byproduct coke plant operations contains relatively high concentrations of phenol, ammonia, oil and grease, and other pollutants of concern. It is expected that significant fractions of these pollutants will also be present in the wastewater treatment sludge.

Process Option 1 - Direct Reduction Process Alternative--

The direct reduction process produces four types of solid residues (Volume III, page 76):

- Direct reduction kiln waste,

- Wastewater treatment sludge,

- Electric arc furnace slag, and

- Electric furnace air pollution control dust.

The direct reduction kiln waste consists of the following components:

- Lime - 0.07 ton/ton of output

- Coal ash - 0.063 ton/ton of output

- Discarded coal* - 0.05 ton/ton of output

- (plus utility solid wastes)

---

*A major part of the larger sized coal particles can be separated from the ash and recycled. Coal fines that cannot be screened from the ash are discarded.

The wastewater treatment sludge is expected to be similar to blast furnace sludge in that the liquid fraction of the sludge would probably contain cyanide, ammonia, phenol, and sulfide. However, there should be very little fluoride present in the wastewater treatment sludge from the direct reduction alternative, since the use of fluorspar as a fluxing agent has been eliminated.

An estimation of the solid-residue generation rate from the direct reduction process is given below (Volume III, page 77):

- Kiln waste - 0.183 ton/ton of steel product
- Wastewater treatment sludge - 0.157 ton/ton of steel product
- Electric furnace slag - 0.21 ton/ton of steel product
- Electric furnace dust - 0.0075 ton/ton of steel product

Total solid residue - 0.558 ton/ton of steel product

Thus, in terms of quantity, the direct reduction process increases the amount of total solid residue generated on site by approximately 86% (0.558 ton/ton of output vs. 0.30 ton for the coke oven/blast furnace/BOP route). However, it should be recognized that a large fraction of the total solid residue is slag, which as previously described, is often recycled for its commercial value in the form of construction material. In addition, the electric arc furnace in the direct reduction route is capable of using scrap iron and steel to a larger extent than the BOP route. With regard to the solid residue actually destined for land disposal from steelmaking, i.e., the wastewater treatment sludge, direct reduction and conventional technology produce very nearly the same solid residue in terms of both quantity and composition.

Summary

The basic oxygen process (BOP) for steelmaking produces two major solid-residue streams; slag and wet sludge from dust collection. The process option involving the combustion of BOP off-gas is not expected to significantly alter the quantity of either the slag or the dust collection sludge. The composition of the dust collection sludge, however, will be slightly altered in that it will be far less oxidized than the dust produced by the base case process and may present somewhat more of a leaching problem.

The base case blast furnace method for producing iron generates the two major solid-residue streams; slag and wastewater treatment sludge. The process option, equipping a blast furnace with external desulfurization, will result in a slight decrease in the solid-residue generation rate. The solid-residue composition in expected to be essentially the same as the base case process.

The conventional method of iron and steelmaking, consisting of a byproduct coke plant, a blast furnace, and a BOP furnace, produces a number of solid-residue streams which consist of coke dust, slags, and wastewater treatment sludges. The process option involving the direct reduction of iron ore eliminates the coke dust, but also produces a number of slags and wastewater treatment sludges. The total quantity of solid residue generated by the direct reduction process is substantially greater than that of the base case; however, much of this is slag which is normally sold for its commercial value. Nevertheless, if one were to assume (namely) that all incremental production achieved in 1989 were obtained by the DR/EAS route, the solid residue would be increased 86% over that for the Coke/Blast Furnace/BOF. A continued market for slag would have to be assured to minimize the effect.

A comparison of the solid-residue discharge is presented in Table 6.

Of the steel industry process options studied, only external desulfurization of hot metal and direct reduction have a significant impact on solid-residue generation with the former achieving a 25% reduction in the solid-residue waste load, while that generated by DR/EAF is, surprisingly, some 86% higher. In both cases, the nature of the solids is not significantly different from that produced by the existing process. Further, the much larger solid residue load from DR/EAF is unimportant as long as slag can be sold for use in construction. Consequently, it does not appear that solid waste will be a significant factor to be considered by the industry in making its choices as to future capital investments.

Of course, the question of electricity generation for the EAF has been discounted. However, in terms of overall environmental considerations, it is not of major importance. For example, if all incremental steel production were to be achieved by DR/EAF, 0.4 quads of electrical energy would be required, compared to 17 quads of purchased fuels used by the utility section in the year 1971.

PETROLEUM REFINING INDUSTRY

Total Petroleum Refining Process

Base Case Solid-Residue Disposal--

For the purpose of performing economic and energy-utilization comparisons, three base case refineries were established in the original study: an East Coast refinery, a West Coast refinery, and a Gulf Coast refinery. The three base case refineries reflect differences in feedstock, process configuration, and product mix. A description of the refinery models used for comparison is presented in Volume IV, pages 21-32. Although the nature and quantity of solid-residues emanating from refineries are highly variable and still the subject of investigation, no difference in solid-residue composition or rate of generation

TABLE 6. SOLID-RESIDUE DISCHARGE FROM IRON AND STEELMAKING

Process	Estimated Discharge Factor (ton/ton of product)	Estimated Change in Discharge Factor (ton/ton of product)	Solid-Residue Discharge (10^6 ton/yr) 1974	1989-1974
Base Case: The basic oxygen process for steelmaking	0.15	0.0	12.3[b]	9.0[a]
• BOP off-gas recovery	0.15	0.0	--	9.0[a]
Base Case: Production of iron in the conventional blast furnace	0.14	0.0	14.0[b]	6.3[a]
• Blast furnace with external desulfurization	0.105	-0.04	--	4.7[a]
Base Case: Wet Quenching of coke	0.0	0.0	0.0	0.0
o Dry quenching of coke	0.0	0.0	0.0	0.0
Base Case: Conventional iron and steelmaking: coke oven and blast furnace and BOP	0.30	0.0	24.6[b]	18.0[a]
• Direct reduction	0.558	+0.258	--	33.5[a]

[a]Based on increment in production from 1974 to 1989: 27.8 million tons of coke, 44.8 million tons of iron, and 60 million tons of steel.

(continued)

TABLE 6. (continued)

[b]Estimated 1974 discharge based on multiplying discharge factor by 1974 production: 62 million tons of coke, 100 million tons of iron and 82 million tons BOP steel.

[c]If all slag is sold as byproduct, the remaining solid residue would be very nearly the same as the base case.

[d]Product refers to coke, iron or steel.

is implied among the three base case refineries. Values given are estimates, intended to reflect general refinery solid-residue quantities and characteristics.

petroleum refinery generates a wide variety of solid-residue streams, many of which contain materials on the EPA toxic substances, or priority pollutants lists. Basically refinery solid-residue streams fall into two main groups: those intermittently generated and those continuously generated.

The intermittent wastes are generally those that result from cleaning within the process areas and off-site facilities of the refinery. The following are typical intermittent waste streams:

- Process vessel sludges, vessel scale, and other deposits generally removed during plant turnarounds;
- Storage tank sediments; and
- Product treatment wastes, such as spent filter clay and spent catalysts from certain processing units.

The annual volume of refinery intermittent wastes is largely a function of the individual refinery waste management and housekeeping practices.

Continuous residues (those requiring disposal at less than 2-week intervals) can be further broken down into two groups: process unit wastes and waste-water treatment wastes.

Major process unit residues include:

- Coker wastes, such as coke fines from delayed or fluidized cokers, and spilled coke from unloading facilities;
- Spent catalysts and catalyst fines from the fluid catalytic cracking units; and
- Spent and spilled grease and wax wastes from lube oil processing plants.

Wastewater treatment wastes include:

- Waste biological sludges from activated sludge units, and
- Dissolved air flotation float.

Typically such wastes are dewatered by means of sludge thickeners, coupled with vacuum filters or centrifuges. The dewatered sludge can then either be land-disposed or incinerated. Low concentrations of

heavy metals, which could affect the level of control required, are usually present in the sludges.

A summary of major refinery solid-residue streams is presented in Volume IV, page 160. Estimated quantities of the various solid-residue streams for the base case refineries are presented in Volume IV, page 29. The total base case refinery solid-residue generation rate is estimated to be approximately 2.07 lb/1000 lb oil.

Process Option 1 - Direct Combustion of Asphalt in Process Heaters--

At present, the asphalt fraction of a refinery's output is usually subjected to several processing steps to make it suitable for sale as a construction material. Asphalt has characteristically been a very low value refinery product. As a result, the processing and sale of asphalt have been more of a least-cost means of disposal rather than an important source of revenue.

Internal refinery heat energy requirements have been filled by combusting portions of the refinery output. By introducing asphalt into the total refinery heat generation system, a greater quantity of higher value fuels is made available to the consumer. A description of the process involved is given in Volume IV, pages 32-43. Thus, while the direct combustion of asphalt does not save energy in an absolute sense, it does improve the overall form value of the refinery product mix. Direct combustion of asphalt is considered to be most potentially applicable to a base case East Coast refinery.

Asphalt contains an appreciable amount of sulfur and ash. The direct combustion of asphalt will result in a significant increase in the amount of pollution control required. The appropriate control technology for asphalt combustion sources is flue gas desulfurization (FGD). A sulfuric acid product is produced from the FGD system, part of which might be used to offset acid requirements for alkylation, depending on acid purity. Alternatively the acid could presumably be marketed.

Implementation of direct combustion of asphalt will not appreciably alter the quantity or characteristics of the base case East Coast refinery total solid-residue stream.

Process Option 2 - Hydrocracking of Heavy Bottoms Alternative--

The purpose of this process (described in detail in Volume IV, pages 43-52) is to convert heavy ends into lighter, more usable fuels. As in the case of direct combustion of asphalt, this alternative is designed to improve the form value of the refinery product mix rather than to conserve energy in absolute terms. It is most likely applicable to a West Coast base case refinery.

Implementation of heavy bottoms hydrocracking will increase the total quantity of refinery solid residue very slightly. This process will require the disposal of a chrome-moly catalyst. It is estimated that a chrome-moly catalyst waste stream will increase the total refinery solid-residue stream by approximately 3% or by 0.061 lb /1000 lb of oil. The catalyst is different.

Process Option 3 - Flexicoking Alternative--

For a variety of process and economic reasons, the Flexicoking process is most applicable to East Coast refineries. Flexicoking, a combination of fluid coking with coke gasification, contributes to energy conservation in two ways:

(1) It frees high-Btu refinery gas for higher priority uses, and

(2) It converts asphalt feed to naphtha and gas oil intermediates which then become available for refining. This represents a portion of crude which otherwise would not be a salable fuel product.

A detailed description of the Flexicoking process is given in Volume IV, pages 52-67.

The use of Flexicoking increases the amount of sulfur that must be removed from gaseous streams. The sulfur in the high-Btu fuel gas is removed using an amine scrubbing system, and the exhaust from that scrubbing system is sent to the refinery gas plant. The hydrogen sulfide in the low-Btu "flexigas" is too low in concentration to be economically scrubbed out, and, therefore, this process includes an integral Stretford unit for sulfur removal. The Stretford unit has a liquid purge stream which contains rather high concentrations of metallic and organic compounds. A typical composition of a Stretford purge stream is shown in Table 7.

The disposal of Stretford purge solution presents a problem. The solution contains compounds that could disrupt the performance of a biological wastewater treatment system should it be discharged to the main refinery wastewater system. It may have to be concentrated first and then disposed of in a lined disposal site, much in the manner of a solid-residue stream.

The Flexicoking process will also produce a solid-residue stream consisting of coke fines. We do not expect that the coke fines will be particularly objectionable in terms of solid-residue disposal.

Overall, the implementation of the Flexicoking process will result in a significant increase in total refinery solid-residue generation. Even excluding the Stretford purge stream (since it is not actually a

TABLE 7. TYPICAL COMPOSITION OF STRETFORD PURGE SOLUTION

Constituent	mg/l
Na_2CO_3	4,700
Sodium anthraquinone disulfonate	700
$NaVO_3$ (sodium meta vanadate	300
Sodium citrate	300
$Na_2S_2O_3$	6,000
Na_2SCN	6,000

solid waste), the Flexicoking process will almost double the base case refinery solid-residue waste generation rate.

Process Option 4 - On-Site Electric Power by Combustion of Vacuum Bottoms--

In this process option (described in detail in Volume IV, pages 67-78), electric power is generated within the refinery rather than purchased from the local power utility. The internal generation of electric power within the refinery does not conserve energy overall, nor does it consume more energy than when power is purchased, assuming that the internal and external power plants would operate at the same efficiencies. In effect, the form value of the asphalt product is upgraded to a higher form of electric power for refinery use.

Overall, the solid-residue stream for on-site power generation by combustion of vacuum bottoms is essentially of the same volume and composition as that of the base case Gulf Coast refinery, to which it would be most applicable, and at which the bottoms would be disposed of by.

Process Option 5 - High-Purity Hydrogen Production Via Partial Oxidation of Asphalt--

This alternative is based on the production of high-purity hydrogen for hydrotreating from vacuum bottoms, using a partial oxidation process. The feedstorck freed up by this approach would then be available for sale outside the refinery in the form of pipeline gas or naphtha. This alternative is considered most applicable to the West Coast base case refinery.

Implementation of partial oxidation of asphalt will slightly increase the total flow rate of refinery wastewater and will therefore slightly increase the quantity of wastewater treatment sludge. In addition, there will be a small solid-waste stream resulting from waste catalyst used in the partial oxidation process. The catalyst would probably contain nickel or iron compounds. The overall increase in solid-waste volume over the base case is quite small (2.18 lb per 1000 lb versus 2.07 lb per 1000 lb for the base case refinery).

Summary

A petroleum refinery employing base case technology generates a number of intermittent and continuous solid-residue streams, most of which are contaminated with petroleum or petroleum products.

All of the process options proposed for the petroleum refining industry have the same theme: use of heavy ends either to generate power or to manufacture more light end, salable product. In both manners the portion of the crude barrel usable as an energy source would be increased. Of the process options, neither direct combustion of asphalt

nor on-site power generation will appreciably affect the base case solid-residue generation.

Hydrocracking of heavy bottoms will result in a slight increase in solid residue by introducing a chrome-moly catalyst. Flexicoking will require the disposal of coke fines that will more than double the base case solid-residue generation rate. Environmentally, the coke fines are not expected to be particularly objectionable. Partial oxidation of asphalt will result in a slight increase in the base case solid-residue generation rate by increasing the amount of wastewater treatment sludge.

A comparison of the solid waste streams is presented in Table 8.

The increase in solid-residue volume is not great, even for Flexicoking. However, increases in metals (catalysts) and, possibly, sulfur will require more sophisticated and more costly pollution control. Nevertheless, it would appear that both load and even undesirable metal pollution would still be less than that produced by generating an equivalent quantity of energy from coal and would seem to offer a desirable short-range increase in available petroleum fuels (and petrochemical feedstocks) with minimal environmental impact. It should not be ignored however, that petroleum refining is a large industry, and even the best of these options from a residues point of view will generate almost 0.04×10^6 tons of solid residues more in 1989 than in 1974.

Consideration of the incremental solid-residue volume, capital cost, operation cost, and energy savings, is shown in the original Petroleum Refinery report (Volume IV).

PULP AND PAPER INDUSTRY

Bleached Kraft Pulping

Base Case Solid-Residue Disposal--

A detailed description of the base case Kraft process is given in Volume V, pages 54-60. In the manufacture of bleached Kraft pulp, a variety of in-plant solid-residue streams are generated. Many of these solid-residue streams are recycled through the manufacturing process either in the form of recovered chemicals or as auxiliary fuel. The residuals from many of these operations evenutally leave the plant as a wet sludge via the wastewater treatment system. The sludge from the wastewater treatment consists largely of wood fiber, inorganic particulate matter, and excess microorganisms from the biological wastewater treatment process. The sludge is usually subjected to mechanical dewatering to reduce its volume prior to land disposal on or near the plant site.

TABLE 8. SOLID-RESIDUE DISCHARGE FROM PETROLEUM REFINING

Petroleum Refining	Estimated Discharge Factor (lb/1000 lb oil)	Estimated Change in Discharge Factor (lb/1000 lb oil)	Solid-Residue Discharge (10^6 ton/yr) 1974	1989++-1974
Base Case: East Coast Refinery Model	2.07	--	1.53+	0.383
• With direct combustion of asphalt in process heating	2.07	0.0	--	0.383
• With Flexicoking	4.01	+1.94	--	0.742
Base Case: Gulf Coast Refinery Model	2.07	--	1.53	0.383
• With on-site electrical power generation	2.07	0.0	1.53	0.383
Base Case: West Coast Refinery Model	2.07	--	1.53	0.383
• With hydrocracking of heavy bottoms	2.13	+0.06	--	0.394
• With partial oxidation of asphalt to produce H_2	2.18	+0.11	--	0.403

+Estimated 1974 discharge based on multiplying discharge factor by 1974 production of petroleum: 740.0 million tons. Thus this calculation assumes all petroleum in U.S. was refined by the process indicated.

++Based on increment in national production of petroleum from 1974 to 1989 of 185 million tons.

Process Option 1 - Alkaline-Oxygen Pulping--

A process description of alkaline-oxygen (A-O) pulping is provided in Volume V, pages 84-85. In terms of pollution control considerations, its most significant feature is that it employs a non-sulfur cooking step which would eliminate the air pollution from malodorous sulfur compounds and greatly alleviate the bleach plant liquid effluent problem.

It is expected that the wastewater effluent flow rate will not be significantly changed as a result of implementing A-O pulping. However, elimination of two of the standard bleach stages should result in approximately a 50% reduction in both BOD and color for A-O compared with Kraft. Since the quantity of sludge produced by a biological wastewater treatment system is proportional to the amount of BOD removed, a reduction in total BOD raw waste load will reduce the quanity of the biological fraction of the wastewater treatment sludge. Implementation of A-O pulping would certainly not adversely affect the overall solid-residue problem (and very likely, may result in a slight reduction in the quantity of solid-residue generated), nor would the composition of the solid waste be adversely affected. However, it would not be realistic to try to estimate the solid-residue load solely on this information.

Process Option 2 - The Rapson Effluent-Free Kraft Process--

The Rapson effluent-free Kraft process is described in Volume V, pages 95-97. It essentially consists of a number of modifications to the conventional Kraft process which are designed to increase the amount of chemical recovery and water recycle. As its name implies, the main environmental advantage of the Rapson process over conventional Kraft processes is the elimination of water effluent from the bleaching step.

A mill using the rapson process would produce significantly less wastewater than a conventional bleached Kraft pulp mill. It is, therefore, anticipated that the quantity of wastewater treatment sludge would also be less. There is introduced, however, a small stream of salt cake (sodium sulfate) leaving the process, which can either be disposed of or sold.

Mechanical Pulping

Base Case Solid Waste Disposal--

Mechanical pulp (i.e., wood reduced to fiber by grinding) is typically combined with chemical fiber and used primarily in the manufacture of newsprint. It is also used in combination with chemical fiber in the manufacture of catalogue paper, construction paper, and other so-called groundwood papers. Wood chips, sawdust, and shavings from sawmills can be used as raw materials.

Solid residue from this process is mostly wastewater treatment sludge, not unlike that produced by Kraft mills (but usually containing a higher proportion of wood fiber and less dissolved solids).

Process Option - Thermo-Mechanical Pulping (TMP)--

In the TMP process, the wood feed is preheated to 130°C for a short period and then reduced to fibers mechanically in a pressurized device.

The incentive to switch to TMP has been the improved fiber properties and an expansion of the wood source base; i.e., the ability to use chips and residual wood. These newer methods of preparing mechanical pulp, therefore, help to dispose of the solid residue that has historically created a major problem in lumber manufacture.

The use of the TMP process increases the BOD load in the raw wastewater stream by an estimated 20%. Since the quantity of wastewater treatment sludge is proportional to the amount of DOB removed in the biological wastewater treatment system, one can expect that the quantity of wastewater treatment sludge will also be slightly increased.

The Manufacture of Newsprint

Base Case Solid-Residue Disposal--

Newsprint is manufactured from blends of mechanical pulp and Kraft pulp. The solid-residue disposal problems associated with these processes have been discussed in the preceding sections.

Process Option - The De-Inking of Old News for Newsprint Manufacture--

The de-inking of old news for newsprint manufacture is a well-established commercial practice. Although the concept of blending recycled fiber with virgin mechanical fiber is not new, it has only recently been introduced for the manufacture of newsprint on a large scale. It was chosen for in-depth technical/economic analysis because the production of newsprint containing de-inked news now accounts for less than 5% of the total newsprint consumed in the United States, and its broader application could significantly reduce both energy usage and pollution.

De-inking is carried out by washing and pulping the old news in either a batch or continuous operation using heat, water, and de-inking chemicals, typically consisting of sodium peroxide, sodium silicate, and detergents. The de-inking chemicals are largely recoverable.

The raw waste suspended solids in wastewater from de-inking operations are significantly greater than for virgin pulps. Thus, the quantity of wastewater treatment sludge generated by de-inking operations will be greater than that from virgin pulp operations. Nevertheless, although it is difficult to quantify, it is clear that, overall, the

implementation of de-inking old newsprint will alleviate the national solid-residue disposal problem by substantially reducing the amount of old news destined for municipal landfills.

Summary

The base case bleach Kraft pulping process produces solid waste in the form of wastewater treatment sludge. The two process options, alkaline-oxygen pulping and the Rapson effluent-free Kraft process, also produce wastewater treatment sludge, but in somewhat lower but unquantifiable amounts.

Thermo-mechanical pulping is expected to produce slightly more wastewater treatment sludge than the base case technology consisting of mechanical pulping. Thermo-mechanical pulping does, however, allow for the greater use of low-grade wood sources that, in many cases, would otherwise become scrap.

While the de-inking of old news for newsprint results in a slight increase in wastewater treatment sludge, it will result in a very significant overall reduction in solid waste by using an existing waste stream as a raw material.

The several processes considered in the pulp and paper industry offer primarily environmental benefits at the plant site, coupled with an expectation of energy savings. While neither energy savings nor solid-residue volume reductions are very great, the combination does make processes such as the alkaline oxidation and the Rapson attractive to the industry.

De-inking of newsprint offers several advantages which also make it attractive even though the de-inking operation generates a wastewater sludge of its own. The conservation of virgin wood and the potential reduction in municipal solid-residue volume are social benefits that should be considered in broadening the use of this technique. However, it should be borne in mine that advancement of this option could have an adverse effect on those municipalities considering energy from solid-residue systems.

OLEFINS INDUSTRY

Production of Ethylene by Ethane Propane Cracking

Base Case Solid-Residue Disposal--

The production of ethylene by ethane propane cracking is a rather complex process involving the pyrolysis of ethane and propane, followed by a series of separation and purification steps. The ultimate products are ethylene, propylene, pyrolysis gasoline, residue gas, and various other hydrocarbon products. A detailed description of the process is presented in Volume VI, pages 16-22.

In the production of ethylene by ethane propane cracking, there are two major solid-residue streams, which are described below:

- Wastewater Treatment Sludge - There are a number of major wastewater streams associated with the production of ethylene. The combined wastewater stream contains a variety of hydrocarbon pyrolysis products, carbonates, sulfates, sulfides, inorganic slats, and suspended solids. The wastewater is typically subjected to suspended solids removal followed by biological treatment. The sludge produced by these treatment processes contains large quantities of relatively inert carbon particulate matter ("coke"), biodegradable solids from the waste microorganisms in the biological treatment system, and many of the previously listed pollutants originally present in the raw wastewater. The sludge is often dewatered by mechanical means prior to landfill.

  It is important to note that ethylene and proylene are the primary feedstocks for many petrochemical production operations. Ethylene production units are, therefore, often integrated into large petrochemical complexes. It is a common practice to combine most of the wastewater streams from the various production units within the petrochemical complex into a single wastewater stream, and then to treat it in a central wastewater treatment facility. Thus, both the wastewater and the sludge from the wastewater treatment facility are a composite of the individual contributions from the various manufacturing operations.

  We estimate that the ethylene plant generates wastewater treatment sludge at a rate of 1.5 lb of sludge per 1000 lb of ethylene produced (calculated from Volume VI, page 107).

- Spent Desiccants - Desiccants are used in certain drying operations in the production of ethylene. The dessicants are solid particles, typically composed of silica gel, alumina, or ceramic molecular sieve materials. The desiccants themselves are relative inert; however, they can be contaminated with hydrocarbons. The dessicant solid-residue stream is quite small and is estimated to be generated at a rate of 0.075 lb per 1000 lb of ethylene produced. It is generally landfilled on site with other solid-residue streams.

Process Option 1 - Ethylene from the Pyrolysis of Naphtha Alternative--

Because of the foreseeable shortage of natural gas and hence the declining availability of ethane and propane, more and more domestic ethylene production is being based on heavier petroleum products. One

option is the pyrolysis of naphtha. Conceptually, naphtha cracking is quite similar to ethylene cracking. A detailed process description is given in Volume VI, pages 22-26.

While the total energy demand for a naphtha cracker is larger on a per-unit ethylene basis, so much more co-product material is produced that the energy consumption per unit of net hydrocarbon product is smaller than for ethylene-propylene cracking.

The production of ethylene from the pyrolysis of naphtha generates the following solid-residue streams:

- Wastewater Treatment Sludge - The composition of wastewater treatment sludge is quite similar to that generated by the production of ethylene from ethane and propane. Due to the increased size of certain process operations, the quantity of wastewater treatment sludge (estimated to be generated at a rate of approximately 2.65 lb per 1000 lb of ethylene production) is about 70% greater than that resulting from ethylene production from ethane and propane (calculated from Volume VI, page 34).

- Spent Desiccant - The composition and quantity of spent desiccant are almost identical to that produced by ethylene production from ethane and propane.

- Recovered Sulfur - Naphtha feedstocks generally contain higher sulfur concentrations than those found in ethane or propane. The sulfur must, therefore, be removed and recovered as an amorphous solid. The rate of sulfur generation is estimated to be 1.16 lb per 1000 lb of ethylene produced (calculated from Volume VI, page 34). If the sulfur cannot be marketed, it must be disposed of in a landfill. Due to its inert nature open storage (disposal) of sulfur is not an uncommon practice.

Process Option 2 - Ethylene from the Gas-Oil Cracking Alternative--

A natural gas-conserving option, ethylene production from gas oil cracking, is also technically quite similar to that of naphtha cracking. A detailed process description is presented in Volume VI, pages 27-31.

The production of ethylene from gas-oil cracking produces the same type of solid-residue streams as the production of ethylene from naphtha; however, the quantities are significantly greater. The solid-residue streams are as follows:

- Wastewater Treatment Sludge - Due to an even greater increase in size of certain process units over the base case, ethylene production from ethane and propane, the quantity of wastewater

treatment sludge is even greater than that produced by naphtha cracking. The estimated rate of sludge generation is approximately 4.9 lb/1000 lb of ethylene produced - which is over three times greater than the base case and almost twice as great as the naphtha-cracking alternative.

- Spent Desiccant - The nature and quantity of the spent desiccant solid-residue stream is the same as in the base case and the naphtha-cracking alternative.

- Recovered Sulfur - As in the case of naphtha cracking, sulfur must be removed during the process, and is recovered as an amorphous solid. Its generation rate is estimated to be approximately 2.1 lb/1000 lb of ethylene produced which is about 1.8 times as great as that generated by the naphtha-cracking alternative.

Summary

The base case production of ethylene via ethane propane cracking generates two major solid-residue streams: wastewater treatment sludge and spent desiccant.

The production of ethylene by the pyrolysis of naphtha also produces a wastewater treatment sludge and spent desiccant. More wastewater treatment sludge is produced than by the base case technology. In addition, a recovered sulfur stream is generated.

The production of ethylene by gas-oil cracking also generates wastewater treatment sludge, spent desiccant, and recovered sulfur, but in substantially greater quantities than in the naphtha pyrolysis process option.

A comparison of the solid-residue streams is presented in Table 9.

Both naphtha and gas-oil processes also generate other potentially marketable hydrocarbon products, so that the Btu yield per ton of feed and the solid-residue load per ton of feed can also be presented on that basis. Although that view is not addressed in this report, it is considered in the original document (Volume VI, page 10-15).

The use of heavier feedstocks to produce the basic petrochemical building blocks, ethylene and propylene, is accompanied by both lower yield of these monomers and increased solid residue. However, additional hydrocarbon products contribute to reduced energy use based on total useable/salable hydrocarbon products.

The sulfur byproduct recovered from the heavier feeds does constitute a new pollutant, but not one which can be considered severe; if all new capacity of ethylene in 1989 were supplied by the worst case, gas oil,

TABLE 9. SOLID-RESIDUE DISCHARGE FROM OLEFIN PLANTS

Production Process	Estimated Discharge Factor (lb/1000 lb)	Estimated Change in Discharge Factor (lb/1000 lb)	Solid-Residue Discharge* (10^6 ton/yr) 1974	1989*-1974
Base Case: Ethylene by ethane-propane cracking	1.58	0.0	0.0205[b]	0.0442
• Ethylene from pyroysis of naptha	2.73[c]	1.15		0.0764[a]
• Ethylene from gas oil cracking	4.98[c]	3.4		0.1394[a]

[a]Based on increment in production of ethylene from 1974 to 1989: 28.2 million tons.

[b]Estimated 1974 discharge based on multiplying discharge factor by 1974 production of ethylene: 13 million tons.

[c]Excludes recovered sulfur which will presumably be marketed.

sulfur production (at 2.1 lb/1000 lb ehtylene) would only be 14.7×10^3 ton/yr, a volume which should be readily salable. For comparison, approximately 11×10^3 ton of sulfur were produced in the United States in 1974 (Bureau of Mines).

AMMONIA INDUSTRY

Manufacture of Ammonia from Natural Gas

Base Case Solid-Residue Disposal--

The manufacture of ammonia is an integrated process with sub-processes of:

- Producing a hydrogen-rich stream from a hydrocarbon or carbon source via reforming or partial oxidation,
- Gas purification, and
- Ammoniation.

The primary raw material for ammonia is natural gas, and about 95% of the ammonia manufactured in the United States is so produced. A detailed process description of the manufacture of ammonia from natural gas is presented in Volume VIII, pages 25-36.

There are two types of solid residue generated in the manufacture of ammonia from natural gas:

- Wastewater treatment sludge, and
- Waste catalyst.

Wastewater treatment sludge results from treating the following wastewater streams associated with ammonia production: raw water treatment plant effluent, cooling tower blowdown, boiler blowdown, compressor blowdown, and process condensate. The total effluent wastewater flow rate is relatively small and, therefore, the quantity of sludge is also expected to be small. The nature and quantity of the sludge depend on the type of treatment employed.

Although we have no quantitative data on the nature of this sludge, it is reasonable to expect that it would contain inorganic particulate matter such as rust, chromium compounds (if chromate corrosion inhibitors are used in the cooling water system), oil and grease, and small amounts of ammonia.

The unrecovered catalyst from the ammonia converter is composed of iron oxide and is generally landfilled.

Due to its small quantity, solid residue is not considered a major environmental problem in the production of ammonia from natural gas.

Process Option 1 - Manufacture of Ammonia from Coal--

Given the shortage of natural gas, and the need for the United States to reduce its dependence on foreign petroleum, serious consideration should be given to basing future ammonia plants on coal. Prior to World War II, nearly all synthetic ammonia production was based on the use of coal to produce synthetic gas for the actual ammonia production step. Since that time, only a small number of ammonia plants based on coal have been built. A detailed description of the process is presented in Volume VII, pages 37-45.

The use of coal greatly increases the quantity of solid residue generated. In addition to the base case solid-residue streams previously described, the manufacture of ammonia via coal gasification generates the following solid-residue streams:

- Slag - A waste slag, largely composed of the ash content of the coal, is produced in the coal gasification step. An elemental analysis of the slag is presented in Volume VII, page 54. The slag contains leachable heavy metals and, therefore, presents a disposal problem. Very large quantities of slag are produced. The estimated rate of slag generation is 0.182 ton per ton of ammonia produced (calculated from Volume VII, page 66).

- Runoff Treatment Plant Sludge - Since large quantities of coal and slag must be stored on-site, contaminated stormwater runoff is a major water pollution problem associated with the coal gasification alternative. The primary pollutants of concern in the runoff water are heavy metals. Therefore the proposed wastewater treatment system consists of precipitation (with lime) and settling. A waste sludge composed of metal hydroxides is generated at an estimated rate of 0.052 ton per ton of ammonia (calculated from Volume VII, page 65).

- Synthesis Gas Purification Wastewater Treatment Plant Sludge- The wastewater from the synthesis gas purification step contains biodegradable material (notably methanol) and hydrogen sulfide. If proper design criteria are followed, it can be treated in a high-detection-time biological treatment system. The biological treatment system will produce a small sludge stream largely composed of waste microorganisms and a certain amount of methanol and sulfide in the liquid fraction. The rate at which this waste is generated is estimated to be approximately 0.0011 ton per ton of ammonia (calculated from Volume VII, page 66).

- Recovered Sulfur - The sulfur removed from the coal during the gasification step is recovered as molten sulfur. In our analysis it was assumed that this byproduct sulfur would be marketed. If market conditions are such that all of the sulfur cannot be sold, it will become a solid-residue stream destined for land disposal. Molten sulfur is expected to be generated at an estimated rate of 0.066 ton per ton of ammonia (calculated from Volume VII, page 64).

Process Option 2 - Production of Ammonia from Heavy Fuel Oil--

This process change is also intended to conserve natural gas. In the early 1950's, industrial processes were developed for producing a synthesis gas, carbon monoxide and hydrogen, by the partial oxidation of hydrocarbons. In producing ammonia from heavy fuel oil, the fuel oil is first converted into synthesis gas which is then processed (in a manner almost identical to that used in the coal gasification alternative) to form a feedstock for the actual ammonia-producing step. A detailed description of the process is presented in Volume VII, pages 66-79.

In addition to the base case solid-residue streams, the following solid-residue streams are generated in the production of ammonia from fuel oil:

- Wastewater Treatment Sludge - There are a number of wastewater streams associated with the production of ammonia from heavy fuel oil. While the exact composition of these streams has not been determined, they do contain biodegradable material and can very likely be subjected to biological treatment in much the same manner as the synthesis gas purification wastewater from the production of ammonia from coal. The rate of sludge generation is estimated to be approximately 0.0015 ton per ton of ammonia produced (calculated from Volume VII, page 77), which is a far smaller amount than the rate of sludge generation for the production of ammonia from coal.

- Recovered Sulfur - As in the case of the production of ammonia from coal, sulfur is removed from the oil and presumably sold as byproduct in the form of molten sulfur. The rate of sulfur generation is significantly less than that for coal gasification (0.0375 ton per ton of ammonia for oil gasification, vs. 0.066 ton per ton of ammonia for coal gasification). If all the sulfur cannot be marketed, a part of it will become a solid-residue stream destined for land disposal.

Summary

The base case production of ammonia from natural gas produces a small quantity of wastewater treatment sludge and unrecovered catalyst.

The production of ammonia from coal produces four solid-residue streams (slag, runoff treatment sludge, synthesis gas purification wastewater treatment sludge, and recovered sulfur) that result in a tremendous increase over the relatively small base case solid-residue generation rate.

The production of ammonia from heavy oil produces two solid-residue streams (wastewater treatment sludge and recovered sulfur) that, while representing a substantial increase over the base case, are considerably smaller than that produced by the coal gasification option.

The various solid-residue streams are compared in Table 10.

It is clear that ammonia production from coal would have a measurable impact on solid-residue generation. The nature of the waste will be that inherent in any coal gasification system. Nevertheless, even if all the incremental ammonia production anticipated for 1989 (12.8×10^6 ton) were to be manufactured from coal, this would consume only 3% of the coal that was mined in 1974 (603×10^6 ton). It cannot be ignored that significant costs will have to be borne by the industry to shift to either of these fuels from natural gas and satisfy anticipated environmental requirements.

ALUMINA/ALUMINUM INDUSTRY

The aluminum industry is comprised of two basic operations: (1) the production of alumina (Al_2O_3) from aluminum-bearing minerals, and (2) the reduction of alumina to aluminum metal. The two operations are usually conducted at entirely separate locations.

Alumina Production

Base Case Solid-Residue Disposal--

At present, the sole technology used to produce alumina in the United States is the Bayer process. It is applicable only to bauxite as a raw material, most of which is imported from the Caribbean, northern South America, and Australia.

In the Bayer process (which is described in detail in Volume VIII, pages 106-118), finely ground bauxite is digested at elevated temperatures under pressure. The digesting liquor contains sodium aluminate and free caustic. After the digestion step, the insoluble components of the bauxite, primarily the oxides of iron, silica, and titanium, are removed by thickening and filtration. The aluminum-containing liquor is then

TABLE 10. SOLID-RESIDUE DISCHARGE FROM AMMONIA PRODUCTION

Production Process	Estimated Discharge Factor (ton/ton of ammonia)	Estimated Change in Discharge Factor (ton/ton of ammonia)	Solid-Residue Discharge---1989[a] (10^6 ton/yr) 1974	1989-1974
Base Case: Ammonia from				
• Natural gas	small (unquantified)	--	small[b] (unquantified)	small (unquantified)
• Coal	0.235[c]	0.235		3.01[a]
• Heavy fuel oil	0.0015[c]	0.0015		0.019[a]

[a]Based on increment in production of ammonia from 1974 to 1989: 12.8 million tons.

[b]Estimated 1974 discharge based on multiplying discharge factor by 1974 production of ammonia: 9.2 million tons.

[c]Excludes recovered sulfur which is expected to be sold as a byproduct.

subjected to a series of precipitation, separation, and calcination steps to yield the final product -- alumina.

The separated solids, known as "red mud," are discarded, usually into large tailing ponds. The quantity of red mud removed from the caustic slurry following digestion varies with the bauxite used and can range from 0.33-2.0 ton (dry basis) per ton of alumina produced. About 0.8 ton per ton of alumina is typical in U.S. plants.

The composition of red mud is presented in Volume VIII, page 121. The solid fraction, in addition to containing the oxides of iron, silica, and titanium, also contains undissolved alumina, phosphates, lime, and manganese oxide. The liquid fraction of the red mud is highly alkaline (typically having a pH of 12.5) and contains high concentrations of caustic, soda ash, sodium chloride, and dissolved alumina.

Process Option 1 - Production of Alumina from Domestic Clays via Hydrochloric Acid Leaching--

The impetus for employing this process is not energy conservation (it actually uses more energy than the base case Bayer process), but rather to reduce the dependence on foreign sources of raw material. The hydrochloric acid and other alternatives to the Bayer process are based on the extraction of alumina from the large reserves of kaolin clay in Georgia and South Carolina.

The hydrochloric acid process is described in detail in Volume VIII, pages 23-30. Briefly, in the hydrochloric acid process, clay is dehydrated, leached with hydrochloric acid, and then settled to separate the residue from the aluminum chloride/iron chloride solution. This solution is then purified with an amine ion exchange system operation to remove the iron chloride, while leaving the aluminum chloride in solution. The aluminum chloride in the solution is crystallized from the solution and decomposed to alumina, and the acid value is recovered.

The primary waste material from this process is the underflow from the series of thickeners. It consists of the acid-insoluble clay fraction and a dilute aluminum chloride aqueous solution. The composition of this waste stream is given in Table 11.

On a dry basis, this waste is generated at a rate of approximately 3.35 ton per ton of alumina (excluding "mine mooth" solid residue) which is about four times greater than the typical 0.8 ton per ton rate for conventional bauxite-refining plants. The main reason for this tremendous increase in solid residue is the low alumina content of kaolin clay as compared to bauxite. The characteristics of the waste are also quite different. Instead of the liquid fraction of the waste being highly alkaline, it is acidic and contains high concentrations of chlorides. This chemical environment is far more conducive to the dissolution of many trace heavy metals than the alkaline conditions present in red mud from bauxite refining.

TABLE 11. COMPOSITION OF WASTE STREAM FROM LEACHING PROCESS

Constituent	Weight Percent
Alumina (undissolved)	12.8
Silica	33.5
Aluminum chloride (soluble)	0.6
Other soluble chlorides (mostly iron)	1.5
Other impurities (Mg, Ti, P, V. SO_x)	2.7
Water	48.9
Total	100.0

Process Option 2 - Production of Alumina from Domestic Clays via Nitric Acid--

Also intended for the extraction of alumina from domestic kaolin clay, the nitric acid process (described in detail in Volume VIII, pages 30-38) involves the following basic steps:

- Calcining the kaolin clay to make the contained alumina selectively available for extraction with nitric acid;
- Leaching the calcined clay with hot nitric acid at atmospheric pressure to produce a solution of aluminum nitric and a suspension of clay insolubles.
- Separating the clay-insolubles from the aluminum nitrate liquor in thickeners;
- Removing the iron and other impurities from the clarified aluminum nitrate liquor by use of a liquid ion-exchange medium;
- Removing the remaining impurities from the iron-free aluminum nitrate liquor by means of vacuum crystallization of aluminum nitrate nonohydrate;
- Recovering the nitric acid and nitrogen oxide values in the form of nitric acid for recycle; and
- Calcining the product alumina.

The primary waste material from this process is the underflow from the series of thickeners, which consists of the acid-insoluble clay fraction and a dilute aluminum nitrate aqueous solution. The composition of this waste stream is given in Table 12.

On a dry basis, this waste is generated at a rate approximately 1.9 ton/ton of alumina which, although lower than that for the hydrochloric acid process, is still about double that of conventional bauxite refining.

The water is acidic, and the pollutants of major concern are the soluble nitrates which, in general, pose more of a threat to groundwater contamination than either the chlorides from the hydrochloric acid process or the alkaline solutions from the conventional bauxite refining process. Neutralization would be necessary as a first step, even if the waste is disposed of by return to the mine or lagooning.

Process Option 3 - Toth Alumina Process Alternative--

The Toth Alumina Corporation (TAC) has been developing a process for the production of alumina and byproducts from clays and other

TABLE 12. COMPOSITION OF WASTE STREAM
(Nitric Acid Process)

Constituent	Weight Percent
Alumina (undissolved)	1.5
Silica	45.0
Aluminum nitrate (soluble)	1.9
Other soluble nitrates	2.2
Water	47.2
Other impurities (Mg, Ti, P, V, SO_4)	2.2
Total	100.0

alumina-containing minerals. The process involves the chlorination of alumina-containing raw materials in the presence of carbon to produce aluminum chloride vapor and other volatile chlorides. These are subsequently purified to remove other metal chlorides and then oxidized to produce alumina and chlorine for recycle. Based on kaolin clays, the steps in the process involve: (1) ore drying and calcination; (2) chlorination in which the aluminum, titanium, and iron present in the ore are carried overhead as volatile chlorides; (3) separation of the chlorides from the aluminum chloride by fractional condensation and distillation; and (4) oxidation of the iron, silicon, and titanium chlorides to their respective oxides for recovery of chlorine for recycle. Finally, the alumina chloride, after separation, is also oxidized to produce alumina and to recover chlorine for recycle. A detailed description of the process is given in Volume VIII, pages 37-49.

The process produces a dry waste stream which contains the rejected materials present in the clay. An estimated composition of the waste stream is given in Table 13.

The rate at which this waste is generated is estimated to be approximately 1.5 ton (dry basis) per ton of alumina.

Although the solid waste streams are produced in an essentially dry state, liquid waste control will very likely involve the recycling of wastewater through the disposal lagoon, so the same type of wet tailing pond situation will be created. As in the case of the hydrochloric acid process, the pollutants of greatest concern are soluble metal chlorides. If conditions are such that there is a wastewater discharge to the environment, the wastewater would probably have to be subjected to neutralization.

Aluminum Production

Base Case Solid-Residue Disposal--

The Hall-Heroult electrolytic reduction process is presently used to produce all of the primary aluminum throughout the world. A detailed process description is presented in Volume VIII, pages 112-118. Basically, the alumina is dissolved in molten cryolite (Na_3AlF_6) in an electrolytic cell wherein aluminum is liberated at the cathode and oxygen at the anode. The oxygen liberated at the anode reacts with the carbon anode to produce CO_2 and CO. Modern Hall-Heroult electrolytic cells are typically steel boxes lined with insulating refractory and carbon. Carbon blocks at the bottom of the cell serve as the cathode in the electric circuit. The anodes are also carbon-suspended in the electrolyte from above.

Minor amounts of solid residues originate from the handling, storage, and feeding of raw and consumable materials (alumina, calcined coke, cryolite, and aluminum fluoride) brought into the smelter. Emissions

TABLE 13. ESTIMATED COMPOSITION OF WASTE STREAM
(Toth Process)

Constituent	Weight Percent
Aluminum (insoluble)	6.0
Silica	73.7
Iron (ferric) oxide	0.8
Soluble chlorides	2.2
Other impurities	6.8
Water	10.5
Total	100.0

of these materials are largely in the form of dust from handling and feeding to the cells and the anode-making operations.

The rebuilding of cells is another source of solid residues from an aluminum smelter. When a cell reaches the end of its useful life and has to be rebuilt, it is removed, dismantled, and rebuilt. This operation generates a good deal of solid rubble and waste solid materials. Most of the refractory internals are impregnated with cryolite and aluminum fluoride. These materials are typically leached to recover the fluorides for reuse. The quantity of this waste also is generally small and varies greatly from plant to plant.

The major solid-residue stream from aluminum production is the result of air pollution control intended for the collection of particulate matter and fluorides. If wet air pollution devices are used, the scrubber water must be treated for the removal of suspended solids and fluorides. Lime treatment is typically used to precipitate the fluorides as calcium fluoride. The rate of sludge generation is estimated to be 15-30 lb/1000 lb of aluminum produced (Volume VIII, page 137).

Process Option 1 - Production of Aluminum by the Alcoa Chloride Process--

Precise details concerning this process are not available. Basically the feed alumina is converted to aluminum chloride by chlorination in the presence of carbon to form volatile aluminum chloride. This, in turn, is purified and fed to an electrolytic cell to produce molten aluminum at the cathode and chlorine at the anode. The chlorine is recycled to the chlorination step.

Various sludges removed from the electrolyte at times might amount to about 5 lb/1000 lb of aluminum. The sludge would be predominantly sodium aluminate contaminated with NaCl/LiCl and would be quite soluble. Purges of unchlorinated alumina from the chlorinator might amount to 30 lb/1000 lb of alumina (Volume VIII, page 66).

Very large amounts of cooling water would be necessary for the Alcoa process. If chromium corrosion inhibitors are used in the cooling water circuits, a wastewater treatment system would be required for the removal of chromium and a waste sludge would be generated at a rate of approximately 4.7 lb/1000 lb of aluminum (calculated from Volume VIII, page 60).

Since the process involves coke making to supply the carbon, it is quite possible that sulfur dioxide will have to be controlled. If so, a calcium sulfate/sulfite sludge would be generated at a rate of approximately 250 lb/1000 lb of aluminum (calculated from Volume VIII, page 67).

The estimated generation rates of solid-residue streams produced by the Aloca process are summarized in Table 14.

TABLE 14. ESTIMATED GENERATION RATES OF SOLID-RESIDUE STREAMS (Alcoa Process)

Solid-Residue Stream	Estimated Generation Rate (lb/1000 lb of Al)
Sludge removed from electrolyte	5.0
Unchlorinated alumina from chlorinator	30.0
Sludge from treatment of cooling water blowdown	4.7
Calcium sulfate/sulfite sludge from sulfur dioxide control system	250.0
Total solid residue	289.7

The rate of solid-residue generation is over 10 times that generated by the base case Hall-Heroult process. It should be noted, however, that more than 85% of the sludge generated is related to sulfur dioxide control. If power plants supplying the conventional Hall-Heroult process plants are required to install sulfur dioxide controls, it would be necessary to allocate an additional quantity of sludge to the Hall-Heroult process. Thus, it is very difficult to compare the solid-residue generation rates on a truly equivalent basis. One comparison can be made: If one assumes 200 x 10^6 Btu/ton, primarily as electricity, used in Hall-Heroult, and accepts 34 lb of sludge, ash, etc., produced at a cola-fired power plant per 10^6 Btu output as electricity, the difference becomes much smaller. Of course, this does ignore the fact that much of the current electricity used in aluminum production is hydroelectric.

Process Option 2 - Refractory Hard Metal Cathodes--

Refractory hard metal cathodes, made from zirconium and titanium carbides and borides and mixtures thereof, have been considered as potential replacements for the conventional carbon cathodes. They exhibit operational and energy conservation advantages.

The use of such cathodes would not appreciably change the base case solid waste disposal problem since the value of the titanium diboride scrap cathode is high enough to warrant recovery of the material for return to the manufacturer.

Summary

The base case technology for the production of alumina, the Bayer process, produces large quantities of alkaline wet sludge which contains a variety of inorganic constituents. All of the options to the Bayer process are based on domestic kaolin clays rather than imported bauxite as the source of alumina. Due to the lower alumina content of domestic kaolin, all of the process options inherently produce more solid residue than the base case technology. The composition of the solid residue from the process options is radically different. Both the hydrochloric acid and the Toth process produce an acidic waste stream high in soluble chlorides, while the nitric acid process produces an acidic waste stream high in soluble nitrates. Land disposal of one form or another would be the only practical disposal approach.

It cannot be denied that the use of options such as the hydrochloric acid or nitric acid leaching of domestic kaolins would have a massive impact on solid-residue generation, both in volume and in nature. Nevertheless, the nation may find it advisable to pursue such routes over the coming years and steps should be taken to assure minimal environmental impact from such mining and processing operations, both from the technical and from the legal or regulatory point of view. Proper restoration and reclamation of mined sites after, presumably, the exhausted, dewatered, and neutralized clays have been returned to

the mines should be considered an integral part of and an integral cost of the processes.

The major source of solid residue from the base case Hall-Heroult process for aluminum production is the sludge produced from treating the wastewater generated by wet air pollution control devices. The sludge contains calcium fluoride.

While the use of refractory hard metal cathodes will not significantly alter the base case solid-residue generation rate, the production of aluminum by the new Alcoa process will have a major effect on both the quantity and nature of the solid residue generated. The Alcoa process would produce a highly soluble process sludge, a cooling water blowdown wastewater treatment sludge, and a large quantity of calcium sulfate/sulfite sludge resulting from sulfur dioxide control. The quantities of these wastes can only be estimated at this time. The process must be more extensively evaluated in order to assess the total environmental impact relative to the conventional process; however, this will remain elusive since existing Hall-Heroult processing uses off-site electrical generation, often hydroelectrical. It will be necessary to assess, on a site-by-site basis, the total environmental impacts of the two processes including control of SO_x emissions and ash at the supplying power plant, particularly if coal is to be the fuel of choice. On such a basis the differenee may become much less significant and cost and energy savings may be the deciding factors.

The quantities of solid waste discharged from the base case alumina/aluminum production methods and their process options are presented in Table 15.

TEXTILE INDUSTRY

Integrated Knit Fabric Mills

Base Case Solid-Residue Disposal--

The base case knit fabric mill produces polyester doubleknit using purchased texturized yarn. It includes the following sequence of operations: (1) yarn is first knitted into fabric in the greige mill; (2) the greige (undyed, unbleached) fabric then goes through a scouring operation to remove knitting oil, followed by dyeing, washing, and spin-drying to remove as much water as possible before hot-air drying. A finish (softener/lubricant) is then applied to the fabric, which is dried and heat-set. Process water is required for the scouring, dyeing, and washing operation, and this is combined into one wastewater effluent.

Solid residue is not a big problem in the textile industry. One type consists of waste fiber in short lengths which accumulates on and around the machining or is filtered out in the waste treatment system. This material is usually stored and periodically disposed of to landfill.

TABLE 15. SOLID-RESIDUE DISCHARGE FROM ALUMINA/ALUMINUM PRODUCTION

Process	Estimated Discharge Factor (ton/ton of Alumina)	Estimated Change in Discharge Factor (ton/ton of Alumina)	Solid-Residue Discharge (10^6 ton/yr) 1974	1989[a]-1974
Alumina Production				
Base Case: Bauxite refining by the Bayer process	0.8	0.0	6.16[b]	8.6
• Hydrochloride acid--leaching of domestic clays	3.35	+2.55		36.0
• Nitric acid leaching of domestic clays	1.9	+1.1		20.4
• Clay chlorination (Toth) process	1.5	+0.7		16.1
Aluminum Production	(ton/ton of Aluminum)	(ton/ton of Aluminum)		
Base Case: Hall-Heroult electrolyte reduction	0.0225[c]	0.0	0.1125[b]	0.158**
• The ALCOA process	0.29	0.2675		2.0
• Use of refractory hard metal cathodes	0.0225[c]	0.0		0.158**
Base Case: Bayer with Hall-Heroult[d]	1.56	0.0	7.8125	10.92

(continued)

TABLE 15. (continued)

Process	Estimated Discharge Factor (ton/ton of Aluminum)	Estimated Change in Discharge Factor (ton/ton of Aluminum)	Solid-Residue Discharge (10^6 ton/yr) 1974	1989[a]-1974
• Clay chlorination (Toth[d] aluminum) and ALCOA chloride)	3.19	+1.63	--	22.33

[a]Based on increment in production from 1974 to 1989: 10.75 million tons alumina and 7.0 million tons aluminum.

[b]Estimated 1974 discharge based on multiplying discharge factor by 1974 production: 7.7 million tons alumina and 5.0 million tons aluminum.

[c]Based on average of estimated range of 0.015-0.030 ton/ton of aluminum.

[d]Based on 1.93 tons alumina per ton aluminum.

**

A second type is the tarry residues that gradually accumulate in the heat-set tenterframes. These residues consist of degradation products from finishing chemicals, and periodically the tenterframes are shut down so that the residues can be removed manually.

There is also very little, if any, biological wastewater treatment sludge generated by most textile mills. The typical textile mill wastewater treatment plant employs a multiple-stage biological treatment system that has a very long detection time. As a result, there is very little accumulation of excess microorganisms in the biological treatment process.

Color in the effluent of textile mills has been considered a pollutional problem in localized areas. Processes for the removal of color employ lime and/or alum precipitation and produce a waste sludge. Although this is an additional solid-residue stream, it is doubtful whether a high percentage of mills will have to perform color removal in the foreseeable future.

Process Option 1 - Advanced Processing--

"Advanced processing," as applied to integrated knit fabric mills, is a term referring to a collection of process changes, plant modifications, and general operation improvements which are designed to conserve both energy and water. Advanced processing consists of the following measures:

- Aqueous size,
- Water conservation,
- Processing at a low liquor/fabric ratio,
- Vacuum impregnation and extraction, and
- Improved finishing techniques.

These are described in detail in Volume IX, pages 28-31.

While advanced processing will diminish the volume of wastewater and therefore the cost of wastewater treatment, it will have virtually no effect on the solid-residue disposal problem.

Process Option 2 - Solvent Systems--

A textile mill based on a solvent system would employ an organic solvent (typically perchlorethylene) instead of water for the various scouring, dyeing, and finishing operations. The solvent is collected and recovered in a central solvent still. The small amount of condensate from the finishing operation and the still represents the only wastewater effluent that may contain traces of solvent and other chemicals. Knitting oils removed in scouring and chemicals from dyeing and finishing remain as residues in the solvent still and are removed as a solid residue for disposal. Although we have no data on either the quantity

or composition of this solid-residue stream, it is quite reasonable to assume that it will contain a certain amount of organic solvent and finishing chemicals.

Since chlorinated organic solvents are far more environmentally objectionable than relatively inert waste textile fibers, the possibility exists that the implementation of solvent systems will have a negative effect on the base case solid-residue disposal problem. Since the residue would be quite combustible, incineration may be the best means of disposal for this waste stream.

Integrated Woven Fabric Mill

Base Case Solid-Residue Disposal--

Woven fabrics require a much longer sequence of processing operation than knit fabrics. Although more complex, the major processes include various combinations of scouring, washing, bleaching, dyeing, and finishing. The combined wastewater stream from the entire operation contains natural and processing impurities removed by hot alkaline detergents, dye material, oil and grease, and inorganic dissolved solids. The wastewater is basically treated in the same way as wastewater from knit fabric mills. The solid-residue disposal problems are similar.

Process Option 1 - Advanced Processing--

Advanced processing for woven fabrics is similar to advanced processing for knit fabrics in that it consists of a collection of process changes, plant modifications, and general operation improvements. The most important process change is the inclusion of a polyvinyl alcohol (PVA) recovery loop which taken the effluent stream from the desizing step and (after ultrafiltration) recycles the concentrated PVA solution back to sizing, and the hot water back to the desizing operation. A process flow diagram of the advanced processing steps for an integrated woven fabric mill is presented in Volume IX, page 50. This operation both conserves energy (in the form of heated water) and reduces the volume of the effluent wastewater stream. Its implementation is not expected to have a significant effect (either positive or negative) on the base case solid-residue disposal problem.

Summary

The base case production of both knit fabrics and woven fabrics produces relatively small solid-residue streams consisting of waste fiber and tarry residues from finishing chemicals. Although the textile industry produces moderate amounts of wastewater requiring treatment, the type of treatment generally employed produces very little, if any, wastewater treatment sludge.

The only process option expected to have an impact on the solid-residue problem is solvent processing. The presence of additional quantities or organic solvents and finishing chemicals in the solid-residue stream may very well render the solid residue more environmentally objectionable and require more sophisticated attention to the disposal option.

It is unlikely that solid residue will be a significant factor in the textile industry's future decisions concerning the process options they plan to pursue. However, in the case of solvent finishing (and even with some dyes and other finishing chemicals in aqueous finishing), the nature of these solid residues, even after biological treatment, may be such as to warrant careful study into the nature of the materials and the acceptability of the disposal techniques being pursued.

CEMENT INDUSTRY

Manufacture of Portland Cement by the Dry Process, Long Rotary Kiln

Base Case Solid-Residue Disposal--

Hydraulic cement is a powder made by burning lime, silica, alumina, iron and magnesia together in a kiln and then pulverizing the product. The processing of raw materials into finished cement follows four steps:

- Crushing,
- Grinding,
- Clinkering, and
- Finishing grinding.

These steps are decribed in detail in Volume X, pages 84-89. The crushing, grinding, and finishing grinding are merely size reduction and material-preparation steps. The heart of the process - and the operation which consumes about 70-80% of the total energy used in cement manufacturing - is the clinkering step. In the clinkering step, the accurately controlled mixture of raw materials reacts chemically at high temperatures in the kiln to produce "clinker," which is subsequently ground into cement.

Since the changes in Portland cement technology and cement industry practices examined in this study have an effect only on the clinkering operation, the analysis of solid-residue implications has also been restricted to the clinkering operation.

The major type of solid residue is the cement dust collected from the kiln by the air pollution control system (usually consisting of fabric filters). The base case plant is a "non-leaching" plant in that the dust is merely discarded rather than leached with water (a process that can generate serious water pollution problems) to reclaim reusable fractions of the cement dust. On the average, cement dust is generated at a rate of approximately 0.15 lb of dust per lb of cement product.

Depending on the mix of raw materials, the dust contains a variety of soluble and insoluble inorganic constituents, the most prevalent being carbonates, oxides, calcium, potassium, chlorides, and sulfates. Usually about 15% of the total dust is soluble in water. Due to the high fraction of soluble species, care should be taken in the disposal of cement dust to minimize groundwater contamination resulting from stormwater runoff and percolation (e.g., disposal into liquid ponds).

Process Option 1 - Equipping the Rotary Kiln with a Suspension Preheater--

A suspension preheater is a modification, or an addition, to a cement rotary kiln. It is attached to the raw feed inlet end of the kiln, totally replacing the preheating zone of the rotary kiln. A detailed process description is given in Volume X, pages 16-34. Essentially, suspension preheating conserves energy by improving heat and mass transfer and making better use of the waste heat in the combustion gases.

As is the case in the base case cement plant, the suspension preheater alternative will produce a waste dust, which probably will also be stored in large piles or holidng ponds. The quantity of dust generated is expected to be substantially less than that of the base case, 0.064 lb per lb of cement versus 0.15 lb per lb of cement. The dust, however, is expected to contain a slightly higher soluble fraction than that generated by the base case cement plant as described in the Cement Industry report.

Process Option 2 - Installation of a Flash Calciner--

The flash calciner is a process operation intended for installation between a rotary kiln and a suspension preheater. Its use has a number of operational and energy conservation benefits, which are described in detail in Volume X, pages 34-40. The quantity of dust loading of the combustion gas stream leaving a flash calciner should be essentially the same as for a comparable suspension preheater.

Process Option 3 - Fluidized Bed Process--

The difference between the fluidized-bed cement-making process and conventional processes is in the high-temperature clinkering step. All of the other steps are essentially identical. The fluidized-bed process has many mechanical, operational, economic, and energy-related advantages over the rotary kiln manufacturing process. Of particular note is that practically any form of carbonaceous fuel can be used in the fluidized bed reactor. Also, current studies indicate that the cement process employing the fluidized-bed cement reactor, with proper heat recovery, requires significantly less total energy than the conventional dry, long rotary kiln. A detailed description of the fluidized bed process is presented in Volume X, pages 40-54.

Cement plants employment the fluidized bed process will produce a waste dust that is estimated to be generated at a rate of 0.03 ton per ton of cement produced (Volume X, page 57) which is about one-fifth of the amount generated by the base case cement plant.

Unlike the base case cement plant, dust generated by the fluidized bed process will consist of relatively high-grade potassium and sodium sulfate, both of which are highly soluble. There are possibilities for selling this material as a byproduct. However, if the material cannot be sold as a byproduct, it will have to be stored on-site in a manner similar to that described for the base case. The high solubility of the material imposes even a stronger need to dike the storage area and to collect and treat runoff water, since dissolved salts are a potential pollution problem.

Process Option 4 - Conversion to Coal Fuel from Oil and Natural Gas--

The energy-conservation potential of the use of coal fuel is primarily one of form rather than quantity of energy. A variety of material-handling steps and process modifications are required to convert a conventional oil- or natural gas-fired rotary kiln to coal. These measures are discussed in detail in Volume X, pages 60-66.

The solid-residue implications associated with the use of coal have to do with the ultimate fate of the ash content of the coal. Typical bituminous coal contains approximately 10% ash by weight. Between 50 and 100% of all of the coal ash produced by the combustion of coal in a rotary cement kiln contacts and chemically combines with the clinkering raw materials, thereby losing its identity as coal ash and becoming Portland cement clinker. When using coal, however, the composition of the raw materials must be adjusted to incorporate the coal ash.

A portion of the coal ash escapes the rotary kiln with the cement dust and is eventually disposed of with the cement dust. It alters the composition of the combined waste, principally due to the presence of heavy metals in coal ash. (A composition of West Virginia coal ash is presented in Volume X, page 73.)

The relative fraction of the coal ash which leaves the plant as cement versus solid waste is highly dependent on the raw material compositions, process configuration, and other site-specific factors. It is, therefore, not possible to quantify, with any degree of confidence, the overall solid-residue implications of using coal as a fuel in cement manufacturing. The 5.7 million Btu of coal required per ton of cement amount to about 0.25 ton of coal containing 250 lb of ash. Up to a half of this ash (125 lb) may be discharged with the flue dust. Thus compared to oil or gas firing, solid residue discharges with coal firing may increase from zero (if the flue dust is recycled) to 0.06 ton/ton of cement.

Summary

The base case dry process, long rotary kiln method of cement manufacture produces a solid-residue stream consisting of cement dust collected as the result of air pollution control.

Two of the process options -- equipping the kiln with a suspension preheater and installation of flash calciner -- result in a smaller amount of cement dust; however, the dust in these cases is expected to contain a higher fraction of soluble inorganic constituents.

The fluidized bed process option is expected to produce a solid-residue stream that is only one-fifth the size of the base case solid-residue stream. The solid residue will consist largley of highly soluble potassium and sodium sulfate.

The process option involving the conversion to coal, while introducing coal ash into the overall process, will not necessarily increase the base case solid-residue generation rate because a high fraction of the coal ash will exit the plant in the product cement. However, the presence of leachable metals, both in the dust and even in the cement itself, should be of some concern, and work is needed to determine whether undesirable metals would, in fact, be removed.

The use of coal to fire cement kilns is a particularly attractive means of conserving more valuable natural gas. Moreover, the impact on the overall national solid-residue problem would be minimal. For example, if all 1989 incremental production of cement were to be achieved by direct firing of coal, the industry would be only using 1% of the coal that was mined in 1974. Incremental solid-residue generation would be significantly less than that produced at the utility.

A comparison of the solid-residue discharge for the various process options is presented in Table 16.

GLASS INDUSTRY

Glass Melting

Base Case Solid-Residue Disposal--

Since glass melting is by far the most energy-intensive portion of the entire glass manufacturing process, downstream finishing operations have not been included in the analysis. The conventional glass-melting furnace is presently fired by natural gas. The major raw materials which make up a soda-lime glass (the most common type of glass) are silica sand, feldspar, dolimite, limestone, and soda ash. A description of the base case glass-melting process is given in Volume XI, pages 17-3.

There are two major solid-residue streams from the conventional glass-melting process, both of which consist of particulates removed

TABLE 16. SOLID-RESIDUE DISCHARGE FROM CEMENT PRODUCTION

Process	Estimated discharge factor (ton/ton of cement)	Estimated change in discharge factor (ton/ton of cement)	Solid-residue discharge (10^6 ton/yr) 1974	Solid-residue discharge (10^6 ton/yr) 1989-1974*
Base case: Dry process, long rotary kiln	0.15	0	11.85[b]	4.1[a]
• Kiln with suspention preheater	0.064	- 0.086		1.75[a]
• Installation of a flash calciner	0.064	- 0.086		1.75[a]
• Fluidized bed cement process	0.03	- 0.12		0.82[a]
• Conversion to coal fuel	0.15-0.21	0-0.06		4.1-5.7[a]

*Based on cement production in 1989 being 27.3 x 10^6 ton greater than in 1974.

[a]Based on increment in production of cement from 1974 to 1989: 27.3 million tons.

[b]Estimated 1974 discharge based on multiplying discharge factor by 1974 production of cement: 79 million tons.

from gaseous streams by air pollution control devices. One solid-residue stream consists of dry particulates which have been removed by bag filters; the other solid-residue stream consists of particulates in the form of a wet sludge removed from a gas scrubbing system. The composition of glass-melting gaseous emissions is presented in Volume XI, page 27. Pollutants of concern in the solid waste (i.e., collected particulate matter) are fluorides, lead, borates, antimony, arsenic, selenium, and other heavy metals. In addition, the liquid fraction of the sludge contains dissolved sulfites and sulfates.

The rate of solid waste generation for a conventional glass-melting operation is estimated as follows (calculated from Volume XI, pages 32,33 and assuming baghouse dust amounts to 1 lb per 1000 lb of glass as in the coal gasification case, Volume XI, page 43):

Baghouse dust	1.0 lb/1000 lb of glass
Wastewater treatment sludge	8.6 lb/1000 lb of glass
Total solid waste generation rate	9.6 lb/1000 lb of glass

Process Option 1 - Melting Energy Supplied by a Coal Gasification System--

In this process change, an on-site coal gasification system is designed to supply the entire fuel gas requirements for the melting operation, thus eliminating the dependence on natural gas. Generally, coal gasification processes include, in some variation, the following steps:

- Coal handling and storage,
- Coal preparation,
- Gasification,
- Oxidant feeding, and
- Gas cleaning.

The details of the process are described in Volume XI, pages 32-45.

The introduction of coal into the system generates two additional solid-residue streams:

- Sulfur removed from the coal, and
- Coal ash.

Thus, implementation of coal gasification increases the quantity of solid residue by about a factor of 4. While the nature of the solid residue will also change, one cannot say that the coal ash exacerbates the need for sound environmental control.

Process Option 2 - Melting Energy Supplied by Direct Coal-Firing--

Direct coal-firing has the advantage over other coal-firing processes in that is uses all of the heating value of the coal. To use coal directly in burners, a coal storage area is needed as well as a live coal storage bin, a pulverizer, screens, a feeder, and the pulverized coal burner(s). A coal storage area capable of storing about one month's supply appears reasonable.

Since coal is a high-sulfur fuel, a direct coal-fired glass melting facility will require a sulfur dioxide scrubbing system. Alkaline-based SO_2 scurbbers generate solid residue in the form of calcium sulfate/sulfite sludge.

Additional solid-residue streams resulting from the direct firing of coal include coal ash, the dust from fabric filters, and wastewater treatment sludge.

The quantity of filter dust and coal ash is approximately the same as that generated by the coal gasification alternative, i.e., 38 lb/1000 lb of glass. The sulfur dioxide scrubber sludge and the wastewater treatment sludge are generated at a rate of approximately 56 lb/1000 lb of glass melted (calculated from Volume XI, page 44).

Process Option 3 - Coal-Fired Hot Gas Generation (COHOGG)--

In this process (which is described in detail in Volume XI, pages 48-53) coal is pyrolyzed to produce a combustible gas for the glass melting operation. Sulfur is removed directly within the process by the addition of limestone. In addition to the ash from the coal (about 37 lb/1000 lb glass) and the base case solid-residue streams amounting to 9.6 lb/1000 lb glass, this alternative generates a solid-residue stream in the form of calcium-sulfate, at a rate of approximately 20 lb/1000 lb of glass (Volume XI, page 53) resulting in a total solid waste stream of 66.6 lb/1000 lb glass.

Process Option 4 - All-Electric Melting--

Molten glass can be heated by the passage of an electric current. Both the design and the operation of an all-electric glass-melting furnace differ greatly from the typical natural gas-fired regeneration furnace. A detailed description of the design and operational differences is given in Volume XI, pages 53-55.

All-electric melting is based on the use of purchased electrical power, and, therefore, there is a shift of some of the environmental problems from the glass manufacturing plant to the electric power generating station.

This process change generates solid residue in the form of dust from the fabric filter and coal ash (at the power plant). The dust and sludge is about the same amount or possibly slightly less than that generated in the base case (9.6 lb/1000 lb glass), and the coal ash is about the same amount as for the other coal alternatives (371 lb/1000 lb glass). Total estimated solid waste discharges are thus 46.6 lb/1000 lb of glass.

Process Option 5 - Batch Agglomeration Preheating--

This process, still in the developmental stage, is designed mainly to prereact the batch ingredients, rather than to conserve energy. A variation of the process proposes to use waste heat for preheating the materials. The preheating step, in itself, does not generate a solid residue stream.

If natural gas is the energy source, both the nature and quantity of the solid residue are estimated to be about the same as the base case. If one of the coal-based alternatives is used, the previously described solid-residue streams will be generated if the fuel utilization efficiency remains constant.

Summary

The base case gas-fired, glass-melting operation produces two solid-residue streams, baghouse dust and wastewater treatment sludge, which contain raw materials particulate matter.

When melting energy is supplied by coal gasification, two additional solid-residue streams are introduced: coal ash and the sulfur removed from the coal. Implementation of coal gasification increases the quantity of solid waste by about a factor of 5.

Direct coal-firing results in yet another solid-residue stream consisting of sulfur dioxide scrubber sludge, and thereby increases the solid-residue generation rate by a factor of 9.

The coal-fired, hot gas generation process option also produces ash and sulfur dioxide removal wastes, but at a lower rate than direct coal-firing.

All-electric melting produces approximately the same solid waste as the base case; however, it does so by shifting some of the environmental problem from the glass plant to the electric power generating station.

A comparison of the solid waste produced by the various options is presented in Table 17.

Thus, if shortages of natural gas develop in the glass industry, use of coal gasification and, possibly, electric melting may be expected over the coming years. Coal-based processes, e.g., gasification, direct-firing, hot-gas generation, will introduce all of the problems inherent in the use of coal, including sulfur or SO_2 removal and coal ash but will reduce the industry's dependence on natural gas. Electric melting will transfer the bulk of the solid-residue problem to the utility, but may be beneficial for its load-levelling effect and may minimize pollution cost and problems by having it done centrally at the utility.

Although the glass industry is considered a major energy consumer, its energy use is only 0.4% of the national total. Thus, the solid-residue volume would constitute only the same small fraction relative to that generated by utilities. However, the industry is relatively concentrated in some geographical areas (e.g., New Jersey) where land disposal of ash for industry -- or for utilities -- is rather limited and the local impact of any coal-based alternative could be more significant on a local or regional basis.

CHLOR-ALKALI INDUSTRY

Chlorine Production Via the Graphite Anode Diaphragm Cell

Base Case Solid-Residue Disposal Problem--

A detailed description of the diaphragm cell process is given in Volume XII, pages 21-28. In this process a nearly saturated solution of sodium chloride is subjected to electrolysis to yield chlorine, sodium hydroxide, and hydrogen. Prior to electrolysis, heavy metals, calcium, and magnesium are removed from the raw brine by adding sodium carbonate and then precipitating the metals as hydroxides and carbonates. The precipitates are removed as a wet sludge and usually sent to a lagoon. It is estimated that brine purification sludge is generated at a rate of 63 lb/1000 lb of chlorine (Volume VII, page 23).

During normal processing the graphite anodes are consumed and form tiny particles which clog the diaphragm cathode. As a result, cells must be periodically rebuilt. The debris from cell rebuilding, asbestos diaphragm material, anode stubs, and cell bodies, are disposed of through landfill dumping. Lead is present in cell bottoms, and thus appears in the total solid-residue stream. The waste material resulting from the rebuilding of electrolytic cells is estimated to be generated at a rate of 3.4 lb/1000 lb of chlorine.

TABLE 17. SOLID-RESIDUE DISCHARGE FROM GLASS FURNACES

Melting unit fuel process	Estimated discharge factor (ton/ton of glass)	Estimated change in discharge factor (ton/ton of glass)	Solid-residue discharge (10^6 ton/yr) 1974	1989-1974*
Base case: Natural gas-firing	0.010	0	0.29[b]	0.130[a]
• Coal gasification	0.050	0.040		0.650[a]
• Direct coal-firing	0.094	0.084		1.222[a]
• Coal-fired hot gas generation	0.066	0.056		0.858[a]
• Electric melting	0.047	0.037		0.611[a]
• Batch preheat with natural gas-firing	0.010	0		0.130[a]

*Based on glass production in 1989 being 13 x 10^6 ton greater than in 1974.

[a]Based on increment in glass production from 1974 to 1989: 13 million tons.

[b]Estimated 1974 discharge based on multiplying discharge factor by 1974 glass production: 29 million tons.

The reactions between chlorine and organic material in the graphite anode lead to the formation of volatile chlorinated organic materials of rather indefinite composition, which must be removed from the product chlorine. This waste stream is generated at an estimated rate of 0.45 lb/1000 lb of chlorine produced, and is usually drummed for disposal by incineration or landfill.

The total solid residue generated by the production of chlorine via the graphite anode diaphragm cell is summarized in Table 18.

Although the brine purification sludge constitutes the largest solid-residue stream, in terms of potential pollution problems it is relatively innocuous when compared to the cell rebuilding waste and the product chlorine purification waste.

Process Option 1 - Dimensionally Stable Anodes (DSA)--

To eliminate the problems associated with the graphite anode, the industry has long worked on developing a non-consumable anode for use in the diaphragm cell. The dimensionally stable anode consists of an expanded titanium metal substrate coated with precious metal/rare earth oxides. The DSA has numerous advantages which result in power savings and reduced pollution loads.

While the brine purification sludge will remain unchanged, DSA-equipped production units will reduce the quantity of cell-rebuilding wastes to approximately 1.2 lb/1000 lb of chlorine (Volume VII, page 62) and, perhaps more importantly, will virtually eliminate the formation of chlorinated organics and the need for their removal from the product chlorine. The total solid residue generated by chlorine production units equipped with dimensionally stable anodes is in Table 19.

Process Option 2 - Modified Diaphragms--

In addition to the significant changes in anodes, some major improvements on diaphragms are being introduced which have beneficial effects on both power consumption and pollution control. The three most significant modified diaphragms are: (1) polymer-modified asbestos, (2) polymer membrane, and (3) ion exchange membranes. These are described in detail in Volume XII, pages 48-52.

Polymer-Modified Asbestos - Use of the polymer-modified asbestos diaphragm has a minor environmental advantage over use of conventional asbestos diaphragms in that the discarded material, at the time of cell rebuilding, is in stablilized pieces instead of loose asbestos fibers. Thus disposal is easier and safer, because the fibers resist dispersion. The amount of brine sludge generated would be the same as in the base case, and the quantity of cell-rebuilding waste would be approximately the same as in the case of the dimensionally stable anode.

TABLE 18. SOLID RESIDUE GENERATED IN PRODUCING CHLORINE VIA GRAPHITE ANODE DIAPHRAGM CELL

Solid-residue stream	lb/1000 lb of chlorine
Brine purification sludge	63.0
Cell rebuilding waste	3.4
Product chlorine purification waste	0.45
Total	66.9

TABLE 19. SOLID RESIDUE GENERATED BY CHLORINE PRODUCTION UNITS EQUIPPED WITH DIMENSIONALLY STABLE ANODES

Solid waste stream	lb/1000 lb of chlorine
Brine purification sludge	63.0
Cell rebuilding waste	1.2
Total	64.2

Polymer Membranes and Ion Exchange Membranes - While the quantity of brine purification sludge would remain the same, the use of polymer membranes and ion exchange membranes would eliminate the graphite and asbestos rubble associated with the rebuilding of conventional diaphragm cells. Also, the generation of chlorinated hydrocarbon wastes would be virtually eliminated. The estimated solid-residue streams are given below:

Solid-Residue Stream	lb/1000 lb of Chlorine
Brine purification sludge	63.0
Cell-rebuilding waste	1.0
Total	64.0

Summary

The process options proposed for this industry may be considered improvements on the basic diaphragm cell electrolysis. As such, they do not reduce the major volumetric source of solid residue (brine purification), but they do have a significant beneficial effect on the smaller, but potentially more serious contributors to the total solid-residue load: the chlorine purification waste (chlorinated organics) and the cell-rebuilding waste (asbestos). These effects, coupled with the energy savings achievable by the use of modified cells, suggest that, while solid residues will not be a determining factor in advancement and/or selection of process options and are not large in national impact in spite of the industry's high production, such approaches should be encouraged, recognizing that the potential beneficial effects are achieved in a somewhat circuitous manner.

A comparison of the solid-residue streams generated by the base case technology and its process options is presented in Table 20. Since the quantity of brine purification sludge is the same in all cases, it has not been included in the comparison.

PHOSPHORUS/PHOSPHORIC ACID INDUSTRY

Furnace Acid - Electric Furnace Production of Phosphorus and Conversion of Phosphorus to Phosphoric Acid

Base Case Solid-Residue Disposal--

Phosphate rock is mined in Florida, Tennessee, and North Carolina, and in the Mountain States of the West. It is converted to commercial end-products either by digestion with sulfuric acid to produce phosphoric acid (the "wet process"), or by reduction to elemental phosphorus in an electric furnace. Most of the phosphorus from the electric furnace is burned in air and the oxides absorbed in water to form phosphoric acid.

TABLE 20. SOLID-RESIDUE DISCHARGE FROM CHLOR-ALKALI PRODUCTION*

Process	Estimated discharge factor* (ton/ton of chlorine)			Estimated change in discharge factor (ton/ton of chlorine)	Solid-residue discharge (10^6 ton/yr)	
	brine purification sludge	other	total		1974	1989-1974**
Graphite anode diaphragm cell	0.063	0.00385	0.0669	0	0.736*	0.796
• Use of dimensionally stable anodes	0.063	0.0012	0.0642	- 0.00265		0.764
• Use of modified diaphragms:						
Polymer-modified asbestos	0.063	0.0012	0.0642	- 0.00265		0.764
Polymer membrane	0.063	0.001	0.064	- 0.00285		0.762
Ion exchange membranes	0.063	0.001	0.064	- 0.00285		0.762

* Estimated 1974 discharge based on multiplying discharge factor by 1974 production of chlorine: 11.0 million tons.

** Based on increment in production of chlorine from 1974 to 1989: 11.9 million tons.

TABLE 20. SOLID-RESIDUE DISCHARGE FROM CHLOR-ALKALI PRODUCTION*

Process	Estimated discharge factor* (ton/ton of chlorine) brine purification sludge	other	total	Estimated change in discharge factor (ton/ton of chlorine)	Solid-residue discharge (10^6 ton/yr) 1974	1989-1974**
Graphite anode diaphragm cell	0.063	0.00385	0.0669	0	0.736*	0.796
• Use of dimensionally stable anodes	0.063	0.0012	0.0642	- 0.00265		0.764
• Use of modified diaphragms:						
Polymer-modified asbestos	0.063	0.0012	0.0642	- 0.00265		0.764
Polymer membrane	0.063	0.001	0.064	- 0.00285		0.762
Ion exchange membranes	0.063	0.001	0.064	- 0.00285		0.762

* Estimated 1974 discharge based on multiplying discharge factor by 1974 production of chlorine: 11.0 million tons.

** Based on increment in production of chlorine from 1974 to 1989: 11.9 million tons.

Although phosphoric acid is the principal commercial end-product of each of the two methods, there is an important difference in the purity of the acid obtained. Phosphoric acid produced via the electric furnace process is essentially a pure chemical that is suitable for detergent, food, and fine chemical uses. Wet process phosphoric acid is not pure; it is suitable for fertilizer manufacture, but not for most other purposes without cleanup.

The key issue in this whole analysis is the fact that the manufacture of phosphoric acid via the electric furnace process has an energy consumption per unit of product that is approximately 5 times that of the wet process. There is, therefore, an incentive to modify the wet process in order to produce phosphoric acid that has a level of purity equivalent to that produced by the electric furnace process.

In the electric furnace process (which is described in detail in Volume XIII, pages 22-34) the phosphate rock is first fed to a direct-fired rotary kiln where it is heated to a temperature of incipient fusion. It is then processed through a screening operation to a suitable size range. The kiln gases must be scrubbed to remove dust and fluorides present in the phosphate rock. The other raw materials, coke and silica, are also dried before they are fed, along with the prepared phosphate rock, into the electric arc furnace. The phosphorus is produced as gaseous P_4 and is then condensed as a liquid. The production of phosphorus and its conversion to phosphoric acid usually occur at different locations. The most common practice is to ship the liquid phosphorus to the point of end-use where it is then converted to phosphoric acid on site.

There are a number of solid-residue streams produced by the overall production of phosphoric acid via the electric furnace process:

Slag - Large quantities of slag are produced by the electric furnace process. Slag is generated at an estimated rate of 7.2 tons per ton of P_4. The slag is sold as a construction material and, therefore, does not become a waste stream destined for disposal.

Wastewater Treatment Sludge - Both the phosphorus manufacturing plant and the phosphoric acid conversion plant produce a variety of wastewater streams which must be treated for the removal of phosphorus, phosphates, fluorides, acidity, and trace heavy metals. The most likely form of treatment is lime precipitation which produces a wet sludge containing calcium phosphate, phosphorus, calcium fluoride, calcium sulfate, and a variety of other constituents. We estimate that wastewater treatment sludge from the production of phosphorus and phosphoric acid is generated at a rate of approximately 0.34 ton per ton of phosphoric acid (as P_2O_5).

Care should be taken to dispose of the sludge in an environmentally acceptable manner. The presence of elemental phosphorus and trace arsenic compounds car result in the low-level occurrence of volatile species such as the phosphorus oxides and arsine, depending upon the chemical environment.

Process Option 1 - Wet Process Production of Phosphoric Acid Followed by Chemical Cleanup--

As previously stated, there are a number of impurities in wet-process phosphoric acid which make it unsuitable for use as detergent phosphate. These impurities include calcium chloride, iron and aluminum salts, carbon and organic matter, and small quantities of a number of heavy metals, such as magnesium, chromium, titanium, manganese, copper, zinc, arsenic, vanadium, and uranium. The acid is saturated in calcium sulfate and has a high content of fine suspended solids. It is difficult to remove these impurities to the degree necessary to meet specifications for food grade or fine chemical phosphate use. A major outlet for phosphoric acid, however, is in the form of sodium tripolyphosphate (STPP), which is used in the manufacture of detergents. Wet process acid can be purified to the degree necessary for this product by a two-stage neutralization cleanup process (see Volume XIII, page 48).

The overall process produces three major solid residue streams: (1) the gypsum sludge from the primary leaching of phosphate rock with sulfuric acid; (2) the wastewater treatment sludge produced in the treatment of gypsum pond overflow water; and (3) the impurities removed by the two-stage neutralization cleanup step.

Gypsum Sludge - On a dry basis, approximately 3.5 ton of gypsum ($CaSO_4H_2O$) are produced per ton of phosphoric acid as P_2O_5 (Reference 2). The gypsum is typically stored in huge impoundments which also serve as water recirculation reservoirs. A substantial fraction of the fluorine originally present in the phosphate rock is discharged along with the gypsum as sodium silicofluoride. This stream also contains free phosphoric acid and is slightly acidic.

Wastewater Treatment Sludge - Since most phosphoric acid plants are located in regions of net precipitation, most gypsum ponds overflow, thereby producing a wastewater stream that must be treated prior to discharge. The wastewater must be treated with lime both to neutralize acidity and precipitate soluble phosphates and fluorides. The rate of sludge generation is estimated to be 0.91 ton per ton of phosphoric acid as P_2O_5 (calculated from Volume XIII, page 39).

Impurities from the Two-Stage Neutralization Cleanup Step - The impurities from the two-stage cleanup steps consist of filter cakes containing sodium silicofluoride in both the liquid and solid phases, phosphoric acid, calcium sulfate, ferric phosphate, aluminum phosphate, and trace quantities of heavy metals. We estimate that this total waste

stream will be generated at a rate of approximatley 0.70 ton per ton of product as P_2O_5 (calculated from Volume XIII, page 55).

The total solid-residue discharge from the wet-process production of phosphoric acid followed by chemical cleanup is given in Table 21.

Process Option 2 - Wet Process Production of Phosphoric Acid Followed by Solvent Extraction Cleanup--

In this process (described in detail in Volume XIII, pages 60-71), phosphate rock is dissolved in hydrochloric acid rather than in sulfuric acid. The crude phosphoric acid thus produced is subjected to a solvent extraction step in which the phosphoric acid is transferred from solution in an aqueous phase to solution in an organic phase, such as normal butanol, leaving behind undesirable impurities, such as calcium chloride, in the aqueous phase. The organic phase can then be contacted in a separate unit with fresh water to yeild a pure solution of phosphoric acid. The calcium chloride brine initially separated from the extraction step also contains hydrochloric acid and solvent which must be recovered.

Since the process is still in the developmental stage, some of the solid-residue streams are not accurately quantified. The most significant difference with respect to solid waste is that a large volume concentrated calcium chloride brine stream (generated at an estimated rate of 1.65 ton of $CaCl_2$ per ton of phosphorus, Volume XIII, page 65) is substituted for a large fraction of the solid gypsum stream produced by the conventional sulfuric acid leaching process. Undissolved inorganic solids separated from the digestor liquor would be impounded in much the same way as in the conventional process. Since much of the solid residue has been converted to calcium chloride brine, the size of the impoundments would be considerably smaller.

Impoundment overflow would have to be treated in much the same way as in the conventional process, i.e., via lime treatment to neutralize acidity and to precipitate fluorides, phosphates, and other inorganics. We expect that this sludge will be generated at a rate that is the same as that for the conventional sulfuric acid leaching process -- 0.91 ton per ton of phosphoric acid as P_2O_5 (calculated from Volume XIII, page 68).

It should be noted that solvent (normal butanol) losses within the process will eventually appear in the liquid fraction of the sludge. If solvent losses are severe, the liquid fraction of the sludge could exert a significant biochemical oxygen demand.

This entire process presents serious water pollution control problems.

Process Option 3 - The Use of Byproduct Sulfuric Acid--

A conventional wet process plant for phosphoric acid consists of

TABLE 21. SOLID-RESIDUE DISCHARGE FROM WET-PROCESS PRODUCTION OF PHOSPHORIC ACID

Solid-residue stream	Generation rate (ton/ton of phosphoric acid) as P_2O_5
Gypsum sludge	3.5
Wastewater treatment sludge	0.91
Impurities from cleanup process	0.70
Total	5.11

two distinct process units. In the first, sulfur is converted to sulfuric acid; in the second, sulfuric acid is used as a reagent to convert phosphate rock to phosphoric acid. Sulfur is a major element of the production of phosphoric acid; and at the right price, a phosphoric acid producer would be tempted to use byproduct sulfuric acid (obtained largely from electrical power plant sulfur dioxide control systems) in place of the sulfur.

While the use of byproduct sulfuric acid will eliminate that part of the pollution problem associated with an on-site sulfuric acid plant, it will have a negligible effect on both the quantity and characteristics of the solid residue produced in the manufacture of phosphoric acid.

Process Option 4 - Strong Phosphoric Acid Processes--

Although these processes (described in detail in Volume XIII, pages 73-75) provide certain operational and economic advantages, it is not apparent that they influence the solid-residue disposal problems one way or another.

Summary

Anticipated growth in the detergent industry can be expected to require significant growth in "clean" high-grade phosphoric acid. The present manufacture of high-grade phosphoric acid via the electric furnace process produces two solid-residue streams: slag, which is sold as a construction material, and wastewater treatment sludge. The wastewater treatment sludge contains calcium phosphate, phosphorus, calcium fluoride, calcium sulfate, and a variety of other constituents.

Although the process option involving the chemical cleanup of wet process phosphoric acid offers significant energy advantages, it produces a gypsum sludge, a wastewater treatment sludge, and impurities from the cleanup step. The overall process results in a 13-fold increase in the base case solid-residue generation rate.

The process option involving wet process production of phosphoric acid followed by solvent extraction cleanup produces a far smaller solid-residue stream than the chemical cleanup process option, but does so partially by producting a large concentrated brine stream. Small amounts of organic solvents may be present in the solid residue.

Since the base case electric furnace process relies on coal (coke) rather than on oil or gas, there may be no incentive for developing or encouraging the alternate, more polluting process. Of course, a complete analysis must also include the incremental solid residues generated at the electric power plant.

The use of purchased by-product sulfuric acid instead of on-site generation of sulfuric acid may come about based on economics alone,

but it does not appear that solid residue or its control will be a deciding factor. Again, the pollution generated by a power plant to produce the steam needed for the wet-acid process and now supplied as a "byproduct" of the sulfuric acid manufacture may, at some future time, also become a factor.

A comparison of the on-site waste discharges is presented in Table 22.

PRIMARY COPPER INDUSTRY

Manufacture of Copper by Conventional Smelting and Refining of Concentrates

Base Case Solid-Residue Disposal--

Copper extraction from sulfide ores is traditionally divided into four segments:

- Mining - where ore containing 0.6 to 2% copper is mined;
- Beneficiation - where the copper-containing minerals are separated from the waste rock to produce a concentrate containing about 25% copper;
- Smelting - where concentrates are melted and reacted to produce 98% pure "blister" copper or "anode" copper (copper 98 to 99% pure requiring further refining); and
- Refining - where blister copper is refined electrolytically to produce 99.9% pure "cathode" copper.

The energy-related process changes considered affect only the smelting and refining portion of copper extraction; therefore, conventional smelting and refining is the base case against which potential process alternatives have been compared in order to evaluate pollution and energy consequences of these process alternatives.

Conventional smelting of sulfide concentrate involves the smelting of concentrates in a reverberatory furnace either directly (green charge smelting) or after roasting (calcine smelting). The mixture of molten sulfides from the reverb is converted to blister copper in converters.

Conventional electrorefining purifies the smelter output to cathode quality copper. A detailed description of the conventional smelting and refining processes is presented in Volume XIV, Appendix A.

There are three major solid-residue streams generated by the conventional smelting and refining of copper, which are described below:

TABLE 22. SOLID-RESIDUE DISCHARGE FROM PRODUCTION OF PHOSPHORUS/PHOSPHORIC ACID

Process	Estimated discharge factor (ton/ton of phosphoric acid (as P_2O_5))	Estimated change in discharge factor (ton/ton of phosphoric acid (as P_2O_5))	Solid-residue discharge (10^6 ton/yr) 1974	Solid-residue discharge (10^6 ton/yr) 1989-1974**
Base case: Electric furnace production of phosphorus and conversion to phosphoric acid	0.34	0	0.476*	0.214
• Wet process production of phosphoric acid followed by chemical cleanup	5.11	+ 4.77		3.219
• Wet process production of phosphoric acid followed by solvent extraction cleanup	0.91 (minimum; could be greater)	+ 0.57		0.573
• Use of byproduct sulfuric acid	Same as conventional wet process plant	-		-
• Strong phosphoric acid process	Same as conventional wet process plant	-		-

* Based on increment in detergent-grade phosphoric acid from 1974 to 1989: 0.63 million tons.

** Estimated 1974 discharge based on multiplying discharge factor by 1974 detergent-grade phosphoric acid: 1.4 million tons.

Slag - Slag is produced in the converter and, after being recycled back to the reverberatory furnace to recover its copper content, it is removed from the reverberatory furnace and disposed of as an inert rock. The slag is mainly an iron silicate, containing about 0.5 to 0.9% copper and small quantities of heavy metals including arsenic, antimony, bismuth, mercury, lead, zinc, selenium, and tellurium.

Large quantities of slag are produced. On the average, slag is generated at a rate of approximately 3 ton per ton of copper produced (Volume XIV, page 26).

Dust Bleed - Flue dusts result from entrained particles and condenses effluents in the gas stream. Typically 3 to 6% of the total weight of solids entering the smelter is evolved as dust. All flue dusts contain copper oxides. Most of the dust is collected by air pollution control devices and then recycled to the reverberatory furnace. Since the dust contains impurities, it is not possible to operate in a total recycle mode, and, therefore, a portion of the dust must be bled from the system. At times, it is economical to process these dusts further in order to recover such metals as zinc, lead, etc. Depending on the composition of the feed, a fraction of the dust generated may be diverted and either sold to other specialized smelters or disposed of as a solid waste. The amount of dust destined for ultimate disposal is estimated to be 0.02 ton per ton of copper (Volume XIV, page 39).

Wastewater Treatment Sludge - In the smelting of copper three major wastewater streams are generated, slag granulation water, acid plant blowdown, and anode casting wastewater. The wastewater is acidic, contains high amounts of suspended solids, and also contains heavy metals. The recommended means of treatment for meeting the 1983 effluent guidelines includes neutralization and sedimentation, both of which produce a waste sludge. The sludge from such a treatment system would contain calcium sulfate and a variety of other inorganic substances.

The estimated rate of wastewater treatment sludge generation is 0.09 ton per ton of copper (calculated from Volume XIV, page 36).

The total solid-residue streams are given in Table 23.

Process Option 1 - Outokumpu Flash Smelting--

Flash smelting (described in detail in Volume XIV, pages 41-44) combines the separate roasting and smelting operations of conventional copper extraction into a combined roasting-smelting process. The heat generated by the exothermic roasting reactions can be used for smelting so that little or no extraneous fuel is needed. A characteristic of this method is that fine-grained concentrates are used and the smelting takes place in suspension, which allows for rapid reaction rates. The major advantage of the method is a reduction in fuel used for smelting and the production of a stream of gas high in SO_2 which is suitable for

TABLE 23. SOLID-RESIDUE STREAM GENERATION RATES (COPPER)

Solid-residue stream	Generation rate (ton/ton of copper)
Slag	3.0
Dust bleed	0.02
Wastewater treatment sludge	0.09
Total	3.11

sulfuric acid manufacture. The Outokumpu flash smelting process produces the same quantity of slag and bleed dust as the conventional smelting and refining of copper.

Since the water pollution control problems are similar to those of a conventional smelter, it is reasonable to assume that if the same recommended treatment technology is applied to the Outokumpu process, the same quantity of wastewater treatment sludge would be generated.

Process Option 2 - The Noranda Process--

The Noranda process combines the three operations of roasting, smelting, and converting of copper concentrates in a single reactor. The heat losses suffered during the transfer of concentrate from the roaster to the reverberatory furnace are suppressed, as well as the heat losses occurring during the transfer of matter from the reverberatory furnace to the converter. In addition, the net heat of oxidation is used for smelting. A detailed process description is presented in Volume XIV, pages 55-70.

The quantity and composition of the solid-residue streams are expected to be very much the same as for the base case conventional smelting and refining process.

Process Option 3 - The Mitsubishi Process--

The Mitsubishi process consists of three metallurgical stages, each of which is carried out in a separate furnace, Thus, there is a smelting furnace for concentrates, a converting furnace to oxidize iron in the matte and make blister copper, and a slag-cleaning furnace. Intermediate products in the molten state move continuously among the respective furnaces which are thus functionally connected with each other. A detailed process description is presented in Volume XIV, pages 71-81. The Mitsubishi process has many of the same energy-conserving advantages as the Outokumpu and Noranda processes.

The quantity and characteristics of the solid-residue stream from the Mitsubishi process are expected to be very much the same as for the base case conventional smelting and refining process.

Process Option 4 - The Use of Oxygen in Smelting--

Copper smelting can be conducted with pure oxygen or by using oxygen-enriched air. Reasons for using oxygen or oxygen enrichment include:

- Increasing processing temperatures and process heat rates;
- Decreasing the nitrogen content of the flue gases (when high SO_2 concentrations are needed) and increasing fuel

efficiency (particularly where waste heat is not recovered); and

- Increasing the specific capacity of furnaces so that production of metal is increased for a given size of reactor.

The quantity and characteristics of the solid-residue streams from a conventional plant are not changed by the use of oxygen in smelting.

Process Option 5 - Metal Recovery from Slag--

In conventional copper smelting, converter slag is recycled to the reverberatory furnace, and all of the slag tapped from the reverberatory furnace is discarded. The copper contained in this discarded slag is lost. The amount of copper lost with the slag is quite significant, about 1.5 to 3% or more of the copper in the feed materials.

Slag can be recovered by two methods: (1) flotation, and (2) slag cleaning in electric furnaces.

Flotation - In flotation the slag is ground in the presence of acid, and copper is recovered via froth flotation. This process converts the slag into fine particles which are then disposed of as a wet slurry into a tailings pond. The water from the tailings pond is recycled.

While the overall quantity of slag is not radically different from that for the base case conventional smelter, the slag is now in the form of very fine particles mixed with water rather than large dry particles. The effect of this change is to make control more complex/costly.

Slag Cleaning in Electric Furnaces - The mechanism by which slag can be recovered in electric furnaces is discussed in Volume XIV, pages 93-95. Aside from reducing the copper content of the slag, this practice does not alter the quantity or the nature of the base case solid-residue streams. If anything, the removal of the copper is beneficial in that potential copper leaching is reduced.

Process Option 6 - The Arbiter Process--

The Arbiter process is one of several potentially applicable hydrometallurgical copper extraction techniques. The basic process (described in detail in Volume XIV, pages 95-106) consists of five separate stages for the treatment of copper concentrates. The copper concentrate slurry is first leached with aqueous ammonia and oxygen. The pregnant solution, after separation of leached solids is sent to a solvent extraction step where copper is selectively extracted with an organic reagent to form a copper-loaded electrolytic solution. Copper is

recovered from the solution via conventional electro-winning. The actual process entails a large number of rather complex material recycle circuits and purification steps.

The Arbiter process produces two major solid-residue streams: gypsum sludge and leach residue.

Gypsum Sludge - During this process, ammonia is recovered from spent ammonium sulfate streams by boiling with lime to yield ammonia and gypsum (calcium sulfate). The gypsum sludge forms a major solid-residue stream. It is estimated that gypsum sludge is generated at a rate of 4.5 dry ton per ton of copper produced in the form of a slurry.

Leach Residue - The process produces a leach residue containing iron oxide, silica, pyrites, bismuth, sulfides, lead, arsenic, and other metals. Its estimated generation rate is 1.3 dry ton per ton of copper produced.

These two waste streams would require storage in lined ponds with a wet top surface to prevent dust emissions during the period the pond is in use and proper cover after the pond is after the pond is abandoned.

Summary

The manufacture of copper by conventional smelting and refining of concentrates produces three major solid-residue streams: slag, dust bleed, and wastewater treatment sludge.

The Outokumpu flash smelting process, the Noranda process, the Mitsubishi process, and the use of pure oxygen do not significantly alter the quantity or composition of the solid-residue generated by the base case technology.

Metal recovery from slag will only slightly decrease the base case solid-residue generation rate.

The Arbiter process produces very large quantities of gypsum sludge which is generated at a rate almost twice that of the total base case solid-residue stream, plus a leach residue high in metals but low in quantity.

A comparison of the solid-residue discharges between the base case and its process options is presented in Table 24.

The alternate pyrometallurigcal process suggested in this study (Outokumpu, Noranda, and Mitsubishi) can be expected to play increasingly large roles in the evolution of the industry but the driving forces will be energy conservation and SO_2 control benefits rather than solid-residue aspects, which are not changed significantly. Use of oxygen and copper recovery from slag will, similarly, advance for reasons other than their impact on solid waste.

TABLE 24. SOLID-RESIDUE DISCHARGE FROM PRODUCTION OF PRIMARY COPPER

Process	Estimated discharge factor (ton/ton of copper)	Estimated change in discharge factor (ton/ton of copper)	Solid-residue discharge (10^6 ton/yr) 1974	1989-1974*
Base case: Conventional smelting and refining of concentrates	3.11	0	4.976**	3.420
• Outokompu flash smelting	3.11	0		3.420
• Noranda process	3.11	0		3.420
• Mitsubishi process	3.11	0		3.420
• Use of pure oxygen in smelting	3.11	0		3.420
• Metal recovery from slag	3.11	slight decrease		3.420
• Arbiter process	5.8	2.69		6.380

* Based on increment in production of copper from 1974 to 1989: 1.1 million tons.

** Estimated 1974 discharge based on multiplying discharge factor by 1974 copper production: 1.6 million tons.

On the other hand, hydrometallurgical processes, such as the Arbiter process, have not proven out to offer the expected energy advantages and do generate large volumes of sludge and leach residue which will require controlled disposal.

FERTILIZER INDUSTRY

The Manufacture of Nitric Acid

Base Case Solid-Residue Disposal--

Of the major fertilizer production activities (excluding the production of ammonia which is covered as a separate industry in Volume VII), the manufacture of nitric acid poses the greatest number of possible conflicts between energy conservation and pollution control. The problem areas are in the control of gaesous nitrogen oxide emissions rather than in the manufacturing process itself.

Nitric acid is an important material in the manufacture of fertilizer-grade ammonium nitrate and explosives. The acid is produced by the oxidation of ammonia, usually under high pressure and temperature, over a platiunum catalyst, forming nitric oxide (NO). The gaseous products from the reactor and oxygen are cooled to form NO_2, and are then sent to an absorption tower to form the acid product.

The only significant pollution problem resulting from the production of nitric acid is the discharge of unabsorbed oxides of nitrogen in the absorption tower tail gas. Other than the usual small quantities of general industrial trash found in all manufacturing facilities, no solid residue is generated by the production of nitric acid.

While each of the several processes available for the control of nitrogen oxide emissions have significant energy and air pollution control implications, none produce a solid-residue stream.

Mixed Fertilizer Plants

Base Case Solid-Residue Disposal--

The base case plant used in this analysis is an ammoniation granulation plant (ammoniation of normal super phosphate) equipped with a natural gas-fired dryer and baghouse filter to control particulate emissions. There are no contaminated process wastewater streams, and the collected particulates actually consist of product material and are recycled back into the process. There are no solid-residue streams.

Process Option 1 - Conversion from Natural Gas to Fuel Oil and Installation of a Wet Scrubber for Air Pollution Control--

Due to the impending shortage of natural gas, there is an incentive to convert drying operations from natural gas to fuel oil. When using fuel oil, however, there is a tendency for baghouse filters to become clogged with products of incomplete combustion. While it may be possible to alleviate this problem by modifying the combustion process and achieving essentially complete combustion, in which case solid waste generation would be the same as the base case. However, it is likely that many plants would require a wet scrubber.

Even though it is possible to recycle scrubber water to a high degree, a certain amount must be purged to prevent the excessive buildup of dissolved solids. The scrubber water would contain ammonia, chloride, fluoride, phosphate, and suspended solids. It would most likely have to be treated with lime to precipitate the fluoride and phosphate as calcium fluoride and calcium phosphate, and to convert ammonium ions to ammonia gas* so that it could be stripped from the wastewater by aeration. The wastewater treatment system would produce a waste sludge, principally composed of calcium phosphate and calcium fluoride, that would be generated at a rate of approximately 1.9 lb/1000 lb of product fertilizer. Since it would contain phosphate and fluoride, as well as some dissolved ammonia, care should be taken in its disposal to avoid groundwater contamination.

Summary

The processes considered to control NO_x emissions from nitric acid manufacture cover varying degrees of economic and energy benefits. Different firms will undoubtedly select one or the other for installation over the coming years. However, solid waste is not generated in any of them and should not be a factor in the decision.

The use of oil in the drying of granular fertilizer will probably require the use of scrubbers in place of baghouse filters. The resultant generation of lime sludge containing fluoride and other pollutants and the added cost of the scrubber and lime treatment system may be a deterrent to such fuel switching by the industry. However, the problem is not one of major national significance and probably should not have high priority.

The solid-residue discharge from the selected segments of the fertilizer industry are presented in Table 25.

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* Ammonia in solution.

TABLE 25. SOLID-RESIDUE DISCHARGE FROM FERTILIZER PRODUCTION

Process	Estimated change in discharge factor ton/ton product	Estimated change in discharge factor ton/ton product	Solid-residue discharge (10^6 ton/yr) 1974	1989-1974
Base case: Nitric acid manufactur without NO_x control	negligible	-	0.0	0.0
• Catalytic reduction	negligible	-		0.0
• Molecular sieve	negligible	-		0.0
• Grand paroisse	negligible	-		0.0
• CDL/Vitak	negligible	-		0.0
• Masar	negligible	-		0.0
Base case: Mixed fertilizer plants with natural gas-fired dryers	negligible	-		0.0
• Better equipment with fuel oil technique	negligible	-		0.0
• Conversion from natural gas to fuel oil (installing scrubbers)	0.0019	0.0019		0.0125*

*Based on increment in production of fertilizers from 1974 to 1989: 6.6 million tons.

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